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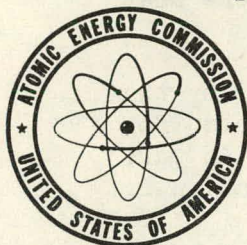
THE RESISTIVITY OF LANTHANUM, CERIUM, PRASEODYMIUM AND NEODYMIUM AT LOW TEMPERATURES

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LANTHANUM, CERIUM, PRASEODYMIUM, AND NEODYMIUM
AT LOW TEMPERATURES

Nancy R. James, Sam Legvold and Frank H. Spedding

I. ABSTRACT

The electrical resistivity of lanthanum, cerium, praseodymium, and neodymium was measured between room temperature and approximately 2°K. The behavior was found to be affected by the method of preparation, the heat treatment, and the crystal structure of the samples, the latter bearing the greatest singificance.

The decrease with temperature of the resistivity of all samples was nearly linear at room temperature in general agreement with theory. At very low temperatures the ideal resistivity, $[\rho]$, of lanthanum and praseodymium was found to obey the empirical equation $[\rho] = aT^b$, where T is the absolute temperature and a and b are constants. In no case was the value of b as high as Bloch's theoretical value of 5.

The face-centered cubic modification of lanthanum was found to possess a much lower resistivity (less than 70 x 10^{-6} ohm-cm.) at ordinary temperatures than the hexagonal close-packed form (approximately 100 x 10^{-6} ohm-cm.). It was hypothesized that the hexagonal form is stable at room temperature and that the face-centered cubic structure undergoes a spontaneous transformation to the hexagonal form. The transformation may be inhibited in extruded specimens. An average superconducting transition temperature was found to be 5.8°K.

The transition in cerium from the normal face-centered cubic to the condensed face-centered cubic modification was found to begin at a temperature between 100 and 120°K. and to be accompanied by a large decrease in resistivity. Great thermal hysteresis was evident. The face-centered cubic crystals may transform into the hexagonal structure at a slow rate which depends upon the rate of cooling from the annealing temperature to room temperature.

An anomalous decrease in the resistivity of cerium which occurred at a temperature between 11 and 14°K. was attributed to a transition from the hexagonal close-packed to the condensed face-centered cubic structure, or possibly, to a condensed hexagonal structure. No hysteresis appeared at these temperatures.

An anomalous decrease in the resistivity of neodymium appeared at approximately 12°K. The effect was possibly explained by a splitting of the lowest energy level of the ion by the field of its neighbors and a consequent re-distribution of the atoms among these states. The increase in the anomaly with successive thermal cycles may be the result of an annealing of the sample during the process of measuring the resistivity.

A comparison of the hexagonal close-packed modification of lanthanum with neodymium indicated that a decrease in resistivity was correlated with an increase in atomic number.

II. INTRODUCTION

The anomalous behavior of some of the rare-earth metals has long been recognized and studied. It has appeared in numerous investigations of the mechanical, thermal, elec-trical, and magnetic properties of the metals and has led to disagreement among investigators which has been furthered by lack of reproducible data. Previous studies make obvious the fact that the purity, heat treatment, crystal structure, and state of strain of the samples all affect the results. Of these, there is no doubt that the crystal structure bears the greatest significance. Because of the occurrence of many of the rare earths in more than one crystalline form, conclusions drawn without knowledge of the structure are likely to be in error.

The metals of the rare-earth series afford a unique opportunity to study the effect on the electronic bands responsible for conductivity caused by a decrease in the atomic radius with successive elements of the series. In this respect, the presentation in this thesis of the electrical resistivity of the first four metals of the series represents a more beginning. Again a knowledge of the crystalline form is necessary and a fair comparison may be drawn only between elements having the same structure.

Purer metals than have ever before been produced may now be obtained. Facilities for obtaining x-ray analyses of the samples were available for this investigation. It was with these facilities at hand and the foregoing thoughts in mind that this investigation was undertaken. The resis-tivity of lanthanum, cerium, praseodymium, and neodymium was measured between room temperature and approximately 2°K.,

and, from the results obtained, an attempt has been made
to integrate the varied information which has appeared in
the literature. The four metals are treated separately in
order to keep the organization of the thesis as simple as
possible. Occasional comparisons between different elements
are made where they are most appropriate.

III. REVIEW OF LITERATURE

A. Lanthanum

1. Crystal structure

Lanthanum has been reported to exist in both the hex-
agonal close-packed and the face-centered cubic forms.
The structure was first reported by McLennan and McKay(1930)
to be hexagonal close-packed with lattice constants $a = 3.72$
and $c = 6.06$ A^o.; and by Quill (1932), with $a = 3.574$ and
$c = 6.063$ A^o. Zintl and Neumayr (1933), using a powder
x-ray method, obtained faint lines indicating a hexagonal
close-packed structure; after annealing the powder for
several days at 350°C. they obtained lines corresponding to
the face-centered cubic system only, with $a = 5.296$ A^o. Rossi
(1934), in repeating the experiment of Zintl and Neumayr,
removed a thin outer layer from the annealed specimen, found
that the latter then gave hexagonal lines, and concluded that
the face-centered cubic structure was a surface phenomenon.
Klemm and Bommer (1937) reported, for the face-centered cubic
form, $a = 5.294$ A^o., in agreement with Zintl and Neumayr.

Considerable information about the crystal structure
has been provided by the work of Ziegler, Floyd, and Young
(1950). Using a powder x-ray diffraction method and four
different samples, they found that hexagonal close-packed
filings, which had been cooled to the temperature of liquid
helium and warmed to room temperature, were still hexagonal.
Filings heated for two days at 254°C. were approximately one-
half face-centered cubic; those heated at 354°C. or higher
were face-centered cubic with only a small amount of the
hexagonal form present. For the cubic form, $a = 5.285 \pm 0.005$A^o.
Filings which had been heated to produce the cubic struc-
ture were, after 130 to 160 days, still face-centered cubic
with no noticeable increase in the amount of hexagonal struc-
ture. When face-centered cubic filings were heated for five
days at 100°C. with the hope of introducing hexagonal close-
packed nuclei, then repeatedly cooled and warmed between-195°C.
and room temperature, they were still face-centered cubic.

On the contrary, filings, taken from bulk specimens which had been heated for four days at 350°C., for four days at 400°C., and for two days at 722°C., still showed lines corresponding to the hexagonal structure. A number of possibilities were suggested to explain this. Filings taken from the bulk specimen may have been converted to the hexagonal form by the strains set up during the filing operation. However, both the filings taken from a chip which had been heated and the chip itself were hexagonal. Insufficient time may have elapsed for the transition to occur. The face-centered cubic structure could have been a surface contaminant, although it was the same whether the sample was heated in a nitrogen or in a helium atmosphere. It may have been a surface effect, although, with more penetrating radiation, the specimens were still cubic. In addition, the dilatometric studies of Trombe and Foex (1943) indicate that the phenomenon is a bulk one. The rate of the transition from the cubic to the hexagonal form in the bulk sample may have been so rapid that it occured while the furnace was cooling.

2. Resistivity

The electrical resistivity of lanthanum has been studied by a number of investigators. Bridgman (1921) reported an approximate value of 59×10^{-6} ohm-cm. for the resistivity of a very impure extruded wire at room temperature. Later (1927), using a sample extruded from metal of high purity, he found the resistivity to be 57.6×10^{-6} ohm-cm. McLennan, Allen, and Wilhelm (1930) measured the resistance of "pure" lanthanum and reported for R/R_o, the ratio of the resistance at any temperature to that at 0°C., 0.520 at 1.9°K.

3. Anomalous behavior

The resistance and specific heat from 200°C. to above 700°C. were studied by Jaeger, Bottema, and Rosenbohm (1938). Maxima in the resistance versus temperature curve appeared at approximately 420 and 560°C.; a change in slope occurred in the range 660 to 715°C. A preliminary heating of the sample at 700°C. completely altered the shape of the curve, an effect which they have attributed to a complete change of the inner structure of the metal during heating. Discontinuities in the specific heat curve, which appeared at 548, 655, and 709°C., were reproducible, independently of previous heatings. Points of discontinuity were shifted approximately 20 degrees lower on the cooling curve.

Anomalies in lanthanum have been reported as a result
of other investigations. Trombe (1934) noted a discontinuity
in the susceptibility, χ, corresponding to 2 per cent of
χ', at 110°K. During the dilatometric studies of Trombe
and Foex (1943), a weak contraction (0.19 per cent in volume)
occurred at 625°K. during the heating of a sample containing
99.2 per cent lanthanum; the corresponding expansion occurred
at 425°K. during cooling. It was concluded that between 78
and 425°K. one form, (α), is stable, that above 625°K.
another form, (β), is stable, and that between 425 and 625°K.
both states coexist. Bridgman (1948), measuring the compres-
sibility of lanthanum, found a volume change of 0.26 per cent
at 23,400 kg/cm².

4. The superconducting transition

The measurement of the superconducting transition tem-
perature, T_s, of lanthanum has led to considerable disagree-
ment. Mendelssohn and Daunt (1937), measuring the suscep-
tibility of a specimen and noting the temperature at which
a strong diamagnetic susceptibility appeared, observed the
transition at 4.71°K. The sample contained 1 per cent iron
and traces of silicon, aluminum, and magnesium. Shoenberg
(1937), using an alternating current method of measuring
the resistance of a specimen whose purity was not reported,
found T_s to be 4.2°K. From the variation with temperature
of the susceptibility of two samples, Ziegler (1948) re-
ported for the first (0.8 per cent iron), T_s = 4.85 ± 0.15°K.;
for the second (1 per cent aluminum, silicon, and tungsten),
T_s = 4.45 ± 0.10°K. The transition occurred over an interval
of less than 0.1 degree.

The data obtained by Ziegler, Floyd, and Young (1950)
are shown, in part, in Table 1. It was thought that the
large increase in T_s caused by heat treatment of specimen
4F was face-centered cubic with a small amount of the hex-
agonal form after the heat treatment and after the low tem-
perature experiment. Since, from the galvanometer deflec-
tion, it was evident that the majority of the sample became
superconducting, it was concluded that probably the face-
centered cubic modification of lanthanum is a superconduc-
tor as is the hexagonal.

In measuring the atomic heat of a sample which, at room
temperature, contained both the hexagonal and the cubic struc-
tures, Parkinson, Simon, and Spedding (1951) found the trans-
ition, not perfectly sharp, at 4.37°K. They found no evi-
dence of an irregularity at 110°K. as was reported by Trombe
(1934).

Table 1

Superconducting Transition Temperatures and
Ranges of Lanthanum

Specimen	As Received Condition		After Heating 4 days at 350°C.	
	T_s	Transition Range	T_s	Transition Range
La 1	5.0°K.	0.1	5.2°K.	0.1
4F	3.9	0.3	5.25	0.3
2S			5.3	0.6 - 0.8
3	4.6	0.1	5.45	0.1

B. Cerium

1. Crystal Structure

The occurrence of two different crystal structures in cerium has long been known. From x-ray powder diffraction patterns, Hull (1921) reported a hexagonal close-packed structure with lattice constants a = 3.65, c = 5.96 Å. and a face-centered cubic structure with a = 5.12 Å., both forms having the same density. Quill (1932) observed only the face-centered cubic form with a = 5.143 Å. Zintl and Neumayr (1933) found for the cubic structure a = 5.139 ± 0.001 Å.; Rossi (1934), a = 5.146 Å. Klemm and Bommer (1937) gave 5.140 Å. for the same constant.

2. Resistivity

Bridgman (1927) reported the resistivity of an extruded sample to be 74.8×10^{-6} ohm-cm. at 30°C. The resistance at low temperatures was measured by McLennan, Allen, and Wilhelm (1930) who reported R/R_0 to be 0.820 at 85°K. and 0.535 at 1.9°K. For the same ratio, de Haas and Voegd (1932) found 0.697 at 1.43°K. Ziegler (1948) reported that a sample containing 2.5 per cent iron was not superconducting above 2°K. On the basis of the atomic volume and the Debye characteristic temperature, de Launay and Dolecek (1947) suggested that cerium should be a superconductor.

3. Phase Transitions

The behavior of cerium at high temperatures was studied by Hanaman (1915) who observed a transition at 490°C. in the cooling curve of a sample containing 96.7 per cent cerium. Jaeger, Bottema, and Rosenbohm (1938) noted, during calorimetric and differential heat capacity measurements, transition points at 362°C. and at approximately 503°C. Values between 320 and 380°C. were not reproducible, but depended upon the previous heat treatment of the sample. The resistance versus temperature curve became reproducible only after repeated heatings of the sample at 540°C., and was characterized by a large increase in slope between 393 and 440°C. The cooling curve was similar in shape although shifted to somewhat lower temperatures. The behavior was thought to be due to a "mosaic structure" of three different forms, each stable within a specified temperature range. Inhomogeneity of the metal was evidenced by thermoelectromotive forces between 350 and 440°C. Loriers (1948), from measurements by differential thermal analysis, attributed the anomalies of Hanaman (1915) and of Jaeger, Bottema, and

Rosenbohm (1938) to the presence of impurities, probably
iron. He observed two transitions, the temperatures of
which did not depend upon the sample; these were at 710
and 740°C. Another occurred at a lower temperature. The
temperature of the latter transition was lower the greater
the iron content of the sample, and appeared to occur at
640°C. for cerium without iron. During cooling, a time
delay was indicated by the occurrence of the transitions
at lower temperatures.

The dilatometric studies of Trombe and Foex (1943 and
1944) showed no anomalies such as those observed by Jaeger,
Bottema, and Rosenbohm (1938) below 500°C. although con-
clusions about the behavior above 450°C. were indefinite
because of the sagging of the sample. Either of two forms
was obtained depending upon the rate of cooling of the sample
from an annealing temperature greater than 500°C. The γ
form, resulting from rapid ("natural") cooling, was charac-
terized by a density of 6.789 g/cm^3 for 99.9 per cent cerium
and by its ability to transform by a contraction of 3.36
per cent in length into the α state at liquid nitrogen tem-
peratures. A cooling rate of 50 degrees per hour from 500°C.
to room temperature invoked an incomplete $\gamma \longrightarrow \beta$ transition
which was accelerated by repeated thermal cycles between
20°C. and liquid nitrogen temperatures. It is assumed that
γ, α, and β correspond to the normal face-centered cubic,
the condensed face-centered cubic, and the hexagonal close-
packed modifications respectively. The first cycle result-
ed in a very slight elongation at approximately -20°C. and,
at liquid nitrogen termperatures, in a contraction one-
third as great as that in the $\gamma \longrightarrow \alpha$ transition. Subsequent
thermal cycles gave smaller contractions at the low tem-
perature and augmentations in volume at room temperature
each time until the behavior became reproducible and the
β form stable at room temperature with a density of
6.74 g/cm^3. It appeared to be impossible for the β
form to transform into the α form at the temperature of
liquid nitrogen. Further heating produced a slight con-
traction at a temperature between 120 and 200°C. The
$\gamma \longrightarrow \alpha$ transition, with a contraction greater than 10 per
cent in volume, was perfectly reproducible irrespective
of the number of thermal cycles; the $\gamma \longrightarrow \beta$ transition be-
came reproducible only after repeated cycles and resulted
finally in a contraction of .0.7 per cent in volume. Both
transitions showed strong thermal hysteresis. The results
were corroborated by the electrical resistance measurements
of Foex (1944). The γ form showed a marked decrease in re-
sistance at -166°C. during cooling; the corresponding in-
crease appeared at -98°C. during heating. The low resis-
tance characterized the α state. The β form showed only a
slight decrease in resistance which was attributed to the

presence, in the form, of a small quantity of γ which was not transformed into β and which was susceptible to giving the form α. Heating to 150°C. produced a slight decrease in resistance corresponding to the transition $\beta \longrightarrow \gamma$.

Bridgman (1927), during compressibility measurements, found a transition evidenced by a permanent change in the dimensions of the sample and corroborated the finding by resistance measurements. The low pressure modification exhibited an anomalous negative temperature coefficient of compressibility and positive pressure coefficient of resistance.

Lawson and Tang (1949) could not induce at liquid nitrogen temperatures a transformation in a sample of high purity which at room temperature was face-centered cubic. Powder diffraction patterns, taken with the sample subjected to a pressure of 15,000 atmospheres, showed that it still was face-centered cubic but with lattice constant a = 4.84 ± 0.03 Å., a decrease which indicated a volume change of 16.5 per cent. The transformation was attributed to a shift of a 4f electron to a 5d orbit. The hexagonal close-packed form appeared upon a sudden release of the pressure and in a period of days gradually transformed into the cubic modification. The transition did not occur in cerium containing 0.2 per cent iron, which at atmospheric pressure was in the hexagonal form.

The diffraction patterns, obtained by Schuch and Sturdivant (1950), of annealed filings indicated the presence of the cubic structure only, irrespective of whether the samples were quenched or cooled slowly to room temperature. However, a transition at the temperature of liquid air could be obtained only with cerium which had been quenched by an air blast from at least 300°C. At 90°K. two phases were present. One was the normally contracted room-temperature form; the other was also face-centered cubic but was anomalously contracted with lattice constant a = 4.82 Å. A smaller proportion of the dense form appeared each time the sample was cooled. The occurrence of the transition was thought to be dependent upon the presence of mechanical stresses.

Measurements by numerous investigators of the magnetic properties of cerium have confirmed the anomalous behavior of the metal. Owen (1912) found, for one sample, a sudden decrease in the susceptibility, χ, at approximately -110°C., although the susceptibility of a second sample increased

steadily with decreasing temperature. A hysteresis loop in a plot of $1/\chi$ against temperature and the apparent existence of two different states were reported by Trombe (1934). Passage from one state to the other occurred at $120^\circ K$. during cooling and at $167^\circ K$. during heating of the specimen. Slight hysteresis was observed by Starr and Kaufmann (1940) at 13.9 and at $20.4^\circ K$. The results were not affected by repeated thermal cycles below room temperature and there was no difference in the measurements at $20.4^\circ K$. whether the sample was cooled from room temperature in one minute or in thirty minutes. Either prolonged aging at room temperature or high-temperature heat treatment produced quantitative, but not qualitative, changes. The susceptibility measurements of Trombe (1944) indicated that the β form of cerium undergoes an extremely reduced hysteresis cycle and the α form, a notably larger one. The behavior was thought to be due, possibly, to a superposition, at low temperatures, of a ferromagnetism caused by iron in the sample on the paramagnetism of cerium. This suggestion was not upheld by La Blanchetais (1945) who, using a sample which contained only 0.0005 per cent iron, obtained results similar to those of Trombe. For the transition $\gamma \rightarrow \alpha$, the contraction in volume of approximately 10 per cent was accompanied by a decrease in magnetic moment of the same order of magnitude.

The atomic heat measurements of two samples of cerium (Parkinson, Simon, and Spedding, 1951) indicate anomalous behavior in the region from 135 to $180^\circ K$. and at approximately $12^\circ K$. Ce I, which at room temperature contained only the face-centered cubic modification, appeared to undergo a transition between 90 and $170^\circ K$. which was marked by great thermal hysteresis. The results were reproducible if the sample was not cooled below $135^\circ K$. After cooling below $85^\circ K$., the results were again reproducible up to $135^\circ K$., but with further heating an anomalous increase in the atomic heat appeared.

Another peak whose height was increased by more rapid cooling in the range from 135 to $85^\circ K$. appeared, centered about $11.5^\circ K$., in the atomic heat versus temperature curve. Ce II, less pure than Ce I and consisting of both the cubic and the hexagonal forms at room temperature, gave irregular results and showed much smaller hysteresis in the 135 to $180^\circ K$. range. The low-temperature peak was centered about $12.5^\circ K$. and again the height was influenced by the cooling rate. The low-temperature anomaly was attributed to a splitting of the lowest energy level of the ion by the field of its neighbors. The behavior at the higher temperature was thought to be due to a transition, perhaps only partial, of the 4f electron to the 5d orbit. The increase in the

low-temperature anomaly was attributed to the inhibition of the transition 4f→5d at high temperatures caused by rapid cooling. A less complete transition produced on successive coolings could explain the lack of reproducibility of the data in the high temperature range.

C. Praseodymium

1. Crystal structure

The crystal structure of praseodymium was reported by Rossi (1934) to be hexagonal close-packed with lattice constant a = 3.652 A^o. and axial ratio c/a = 1.61. Heat treatment at 330°C. for several days did not induce the cubic modification as was the case with lanthanum. After annealing the sample at 750°C. for 48 hours, he obtained photographs which were slightly different but which did not correspond to the cubic form. Bommer (1939) found for hexagonal close-packed praseodymium a = 3.662, c = 5.908 A^o., a structure somewhat distorted from the true hexagonal close-packed. Klemm and Bommer (1937) reported for the face-centered cubic form a = 5.151 A^o. By heat treating a face-centered cubic sample between 300 and 425°C. they (1939) could obtain the hexagonal form. They could not convert the hexagonal modification to the face-centered cubic by heating to these temperatures. Lawson and Tang (1949), by the application of pressure, could not invoke in praseodymium a transformation similar to that which occurred in cerium.

2. Resistivity

The electrical resistivity of an extruded wire whose structure was not determined was reported by Bridgman (1927) to be 69 x 10^{-6} ohm-cm. at 30°C. On the basis of the Debye temperature and the atomic volume, de Launay and Dolecek (1947) suggested that praseodymium should become superconducting.

3. Anomalous behavior

No irregularities in the magnetic susceptibility have been found. Owen (1912) reported a steadily increasing value of χ with decreasing temperature. The Plot of $1/\chi$ against temperature given by Klemm and Bommer (1939) was perfectly linear.

The atomic heat versus temperature curve obtained by Parkinson, Simon, and Spedding (1951), who used a sample which at room temperature was hexagonal only, showed a slight dip at 100°K. The slope of the low-temperature portion of the curve was considerably greater than that of lanthanum, cerium, or neodymium. No hysteresis appeared.

D. Neodymium

1. Crystal structure

Quill (1932) reported for neodymium the hexagonal close-packed structure with lattice constants a = 3.657, c = 5.880 A°. For the same structure Klemm and Bommer (1937) found a = 3.655, c = 5.880 A°. No x-ray evidence has been obtained to show that neodymium exists in another crystalline form.

2. Resistivity

For an extruded wire containing a large amount of magnesium, Bridgman (1921) reported the electrical resistivity to be 107×10^{-6} ohm-cm. On the same basis as that for cerium and praseodymium, de Launay and Dolecek (1947) predicted that neodymium should be a superconductor.

3. Anomalous behavior

Discontinuities in the heat capacity curves of Jaeger, Bottema, and Rosenbohm (1938) appeared at approximately 515 (450 on the cooling curve), 655, and 710°C. Hysteresis occurred between 420 and 530°C. The curves were more reproducible after repeated thermal cycles. A transformation point became apparent at approximately 508°C. A thermoelectromotive force appeared between 500 and 715°C. and the resistance curve showed a large peak at approximately 550°C. The anomalies were attributed to a transition beginning at 510°C., ending at 540°C., from the hexagonal close-packed to the face-centered cubic structure. It may be noted that this is the only mention made in the literature of the existence of neodymium in the face-centered cubic form. However, x-ray evidence was not obtained.

Two peaks were centered at about 7 and 19°K. in the atomic heat curve obtained by Parkinson, Simon, and Spedding (1951) whose sample was entirely hexagonal close-packed at room temperature. As in the case of cerium and praseodymium,

the anomalies were attributed to a splitting of the states
of the 4f electron by the crystal field. No irregularity
appeared at 110°K. as reported by Trombe (1934), who found
a change in slope in the $1/\chi$ versus temperature curve. The
measurements by Owen (1912) of the magnetic susceptibility
indicated a steady increase of χ with decreasing temperature.

IV. APPARATUS AND GENERAL TECHNIQUES

Measurements were taken between room temperature and ap-
proximately 2°K. with the samples and thermometers mounted
just above the bottom of the experimental chamber of a Col-
lins Helium Cryostat. The electrical leads were brought
out through brass cylinders threaded into a plexiglass plate
at the top of the cryostat. One lead was brought through
each cylinder and soldered to it, and the brass was sealed
to the plate with plexiglass glue and glyptal. A neoprene
gasket provided the seal between the plexiglass and the cry-
ostat itself.

The rate of cooling was controlled by varying the engine
inlet pressure; the heating rate, by varying the power sup-
plied to two 400 ohm - 10 watt resistors mounted below the
sample holder. The length of time required to cool the
apparatus averaged 7½ hours; heating occurred over an ave-
rage period of 45 hours. The long heating period was due,
in part, to the inability to maintain thermal equilibrium
while warming the cryostat more quickly.

Temperatures between 300 and 15°K. were determined by a
four-lead standard platinum resistance thermometer, No.
718171, made by Leeds and Northrup Co. and calibrated to
10°K. by the National Bureau of Standards. The #26 B. and
S. platinum leads were connected to #30 B. and S. cotton-
covered copper leads, all junctions being made at the same
place to eliminate thermoelectromotive forces. Below 15°K.
a four-lead constantan resistance thermometer was used.
The thermometer winding consisted of #30 B. and S. cotton-
covered wire, wound loosely, in order to be strain free, and
non-inductively on Bakelite micarta tubing. The leads were
of #24 B. and S. enameled constantan wire which was further
protected by insulating spaghetti. The constantan thermome-
ter was calibrated between 25 and 10°K. against the platinum
thermometer, at 4.2°K. by immersion in liquid helium at at-
mospheric pressure, and at 2.2°K. The lowest temperature
was obtained by reducing the pressure on the helium until
the liquid reached its λ point. Temperatures below 15°K.

were then obtained from the resistance versus temperature
curve. Throughout the range of calibration the curve was
smooth; from 24 to 10°K. it was linear with a sensitivity
of 0.027 ohm per degree. The calibration, repeated several
times during successive experiments, remained essentially
constant below 15°K., the range in which the thermometer
was used.

The resistance of the thermometers was read on a Rubi-
con Mueller Type G2 temperature bridge. A commutator for
interchanging the thermometer leads made the bridge readings
independent of lead resistance. Thermometer readings were
taken both before and after the measurements of the poten-
tial drop across any sample and the mean temperature was
taken to be that of the sample when its resistance was measured.
Above 40°K. temperatures were read to the nearest degree since
the cooling rate was too high to insure thermal equilibrium.
Below 40°K., where the cooling rate was considerably lower,
temperatures were read to the nearest one-tenth of a degree.
For consistency, temperatures were read to the same degree
of accuracy during heating.

The metals used were prepared by a bomb reduction tech-
nique (Spedding, Wilhelm, Keller, Ahmann, Daane, Hach, and
Ericson, 1952) in which the rare-earth chloride is reduced
with calcium metal, with iodine and calcium as a booster.
The reductions were performed in magnesium oxide crucibles,
the excess calcium being distilled, after reduction, from
the rare-earth metal by heating in a vacuum to a temperature
between 1200 and 1250°C. Rods for the experiments were
either cast or extruded from the pure metal. The casting
process consisted of heating the metal in a tantalum-lined
funnel of magnesium oxide and allowing the metal to run into
a 3/8 inch magnesium oxide tube, the process being done in
a vacuum. The extruded rods were 1/4 inch in diameter. All
rods were turned on a lathe to approximately 0.140 inch in
diameter, cut to 2 inches in length, and with the exception
of La II were annealed for 19 hours at 600°C. The length of
the cooling period after heat treatment was, in most cases,
3 hours. The samples were generally stored in a helium at-
mosphere in soft glass tubes although for a short time they
were kept under mineral oil.

Spectrographic analysis showed that all specimens con-
tained less than 1 per cent magnesium, less than 0.025 per
cent calcium, and less than 0.01 per cent other rare earths.
The iron content varied with the specimen. Samples for the
x-ray analyses were cut from the rods and filed to the shape
of needles approximately 0.02 cm. in diameter. More specific
details are given later.

The sample holder contained clamps for three rods and space for the two thermometers. The thermometers, placed as close together as possible, were approximately one-half inch from two of the samples and one inch from the third. As originally built, brass clamps, screwed to an insulating base of phenolic sheeting, held the rods rigidly and were used for current connections to the samples. Connections for measuring the potential drop across the samples were compression springs made of #20 B. and S. copper wire. That part of the spring making contact with the rod was filed to a wedge shape. The leads were #20 B. and S. plastic-covered copper. Before the rods were mounted in the holder, the oxide coating was removed with fine sandpaper and crocus cloth. The diameter was determined with a micrometer caliper and the mean of six readings was used in the calculations. The separation of the potential leads was marked by dividers and estimated to the nearest 0.01 cm. The mean of three readings, with a probable error never greater than ±0.01 cm., was used in the calculations. No correction was made for the change in length due to temperature variation. The holder is shown in Figure 1a.

Although this holder was used for the majority of the experiments, it was unsatisfactory for cerium. At a temperature near that of liquid nitrogen, where cerium experiences a large contraction in volume, a potential contact was frequently broken. Consequently, some of the data are incomplete. To eliminate this trouble, the holder was rebuilt. The brass clamps were changed to rigid wedges against which the rods were forced by small brass springs under tension. The potential leads were changed to #36 B. and S. copper wire in order to decrease the heat leak into the experimental chamber. Although this holder was satisfactory, it could have been improved by the use of springs for the current connections and fixed wedges for the potential contacts. This change would have eliminated the necessity of repeatedly measuring the distance between the potential contacts and would have enabled a more accurate method of measurement to be employed.

A selector switch permitted any one sample to be connected in series with a standard resistance of 0.1 ohm, a rheostat for adjusting the current, a reversing switch, and a 6 volt direct current source. Three storage batteries, connected in parallel in order to insure a more uniform current, were used for the supply. A current of approximately 1/2 ampere was sufficient to give a measurable potential drop across the samples at all temperatures. A second switch permitted the potential leads from the same sample or from
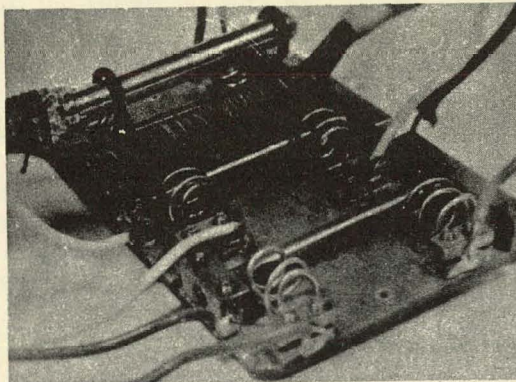
Fig. 1a--Sample holder showing
         three samples and the
         platinum thermometer
         mounted just above the
         constantan thermometer.

the standard resistor to be connected to a Rubicon Type B potentiometer. The potential drop across the rod was compared to that across the standard resistor. Readings were taken with the current in the normal and in the reverse direction in order to eliminate effects due to the junctions, and the mean values were used. Where feasible, several readings were taken with the current in each direction in order to permit the calculation of a probable error in the resistivity. From these data and the dimensions of the sample, the resistivity was calculated.

The size of the symbols on the graphs is indicative of the maximum calculated probable error, $\pm 0.6 \times 10^{-6}$ ohm-cm. In only two cases was the error this large, a more common value being $\pm 0.2 \times 10^{-6}$ ohm-cm. Probably the greatest source of experimental error lay in the maintenance of thermal equilibrium between the specimens and the thermometers. Cooling rates of 2 degrees per minute were not uncommon within certain temperature ranges, and because of the much smaller heat capacity of the thermometers it would be expected that they would respond to a temperature change more rapidly than would the rods. Doubtless conditions during heating more nearly corresponded to those of thermal equilibrium and consequently more weight was given to those points in drawing the curves.

V. RESULTS AND DISCUSSION

A. Lanthanum

1. History of the samples

Two specimens of lanthanum were studied. La I was cast, annealed immediately after casting, and reannealed after the second series of measurements; La II was extruded and given no heat treatment other than that required by the extrusion process. The iron content of La I was 4200 parts per million and of La II, 85.5 parts per million. The densities of the two samples were 6.08 and 5.98 g/cm^3 respectively. A more accurate determination of the densities was not possible because of slight irregularities in the rods.

2. Crystal structure

X-ray analyses, made after the last series of resistivity measurements, indicated the presence in each specimen

of both the hexagonal close-packed and the face-centered cubic structures with a small amount of the oxide, La_2O_3. The amount of oxide present in the original rods was small. However, in preparing the needle-like samples for the x-ray analyses some surface oxide was formed. Probably with time this oxide penetrated to some extent into the interior of the metal. Probably this was greater in the small x-ray samples than in the bulk specimens because of the greater ratio of surface area to volume of the former. Furthermore, the needles were taken from the ends of the rods where oxidation is most rapid. In any case, whatever oxide was present in the bulk specimens would have behaved as a small impurity.

La I was 67 per cent hexagonal with lattice constants a = 3.74 and c = 6.03 A°., and 33 per cent face-centered cubic with a = 5.28 A°. La II was 55 per cent hexagonal with a = 3.77 and c = 6.04 A°., and 45 per cent cubic with a = 5.27 A°. La I appeared to contain more oxide than did La II. Identical results were obtained with samples whose surfaces had been etched and with others which had been filed. It may be noted that the filing operation does not have an important effect on the structure as was thought possible by Ziegler, Floyd, and Young (1950).

3. Resistivity above the superconducting transition temperature.

The variation of resistivity with temperature above the superconducting transition is that of a normal metal. At room temperature the curves are nearly linear in general agreement with theory. Data obtained above 40°K. are shown in Figures 1 and 2. In these figures and in all others showing the resistivity throughout the entire temperature range, the broken curves represent data which are presented elsewhere. At very low temperatures it has been found that the ideal resistivity of many metals obeys the empirical equation $[f] = aT^b$, where T is the absolute temperature and a and b are constants. According to the Bloch theory, b should have the value of 5. The calculated values of a and b for lanthanum are shown in Table 2 and, as may be seen, the values of b are considerably lower than the theoretical value. The data are shown in Figures 4 and 5. The necessary extrapolation of the curves to 0°K. in order to determine the residual resistivity has doubtless introduced some error.

From a comparison of Figure 1 with Figure 2, it is apparent that there is a marked difference in behavior of the two specimens. Several hypotheses exist to explain this
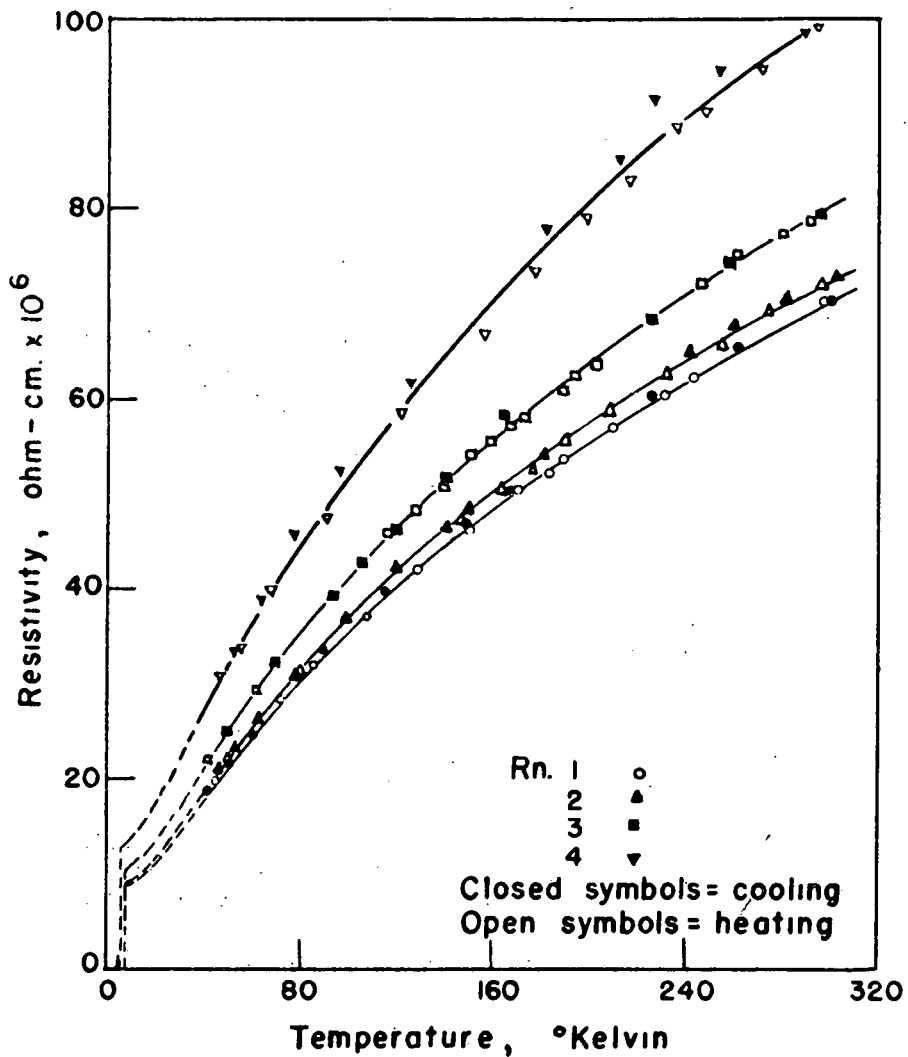
Fig. 1--Resistivity of Lanthanum I as a function
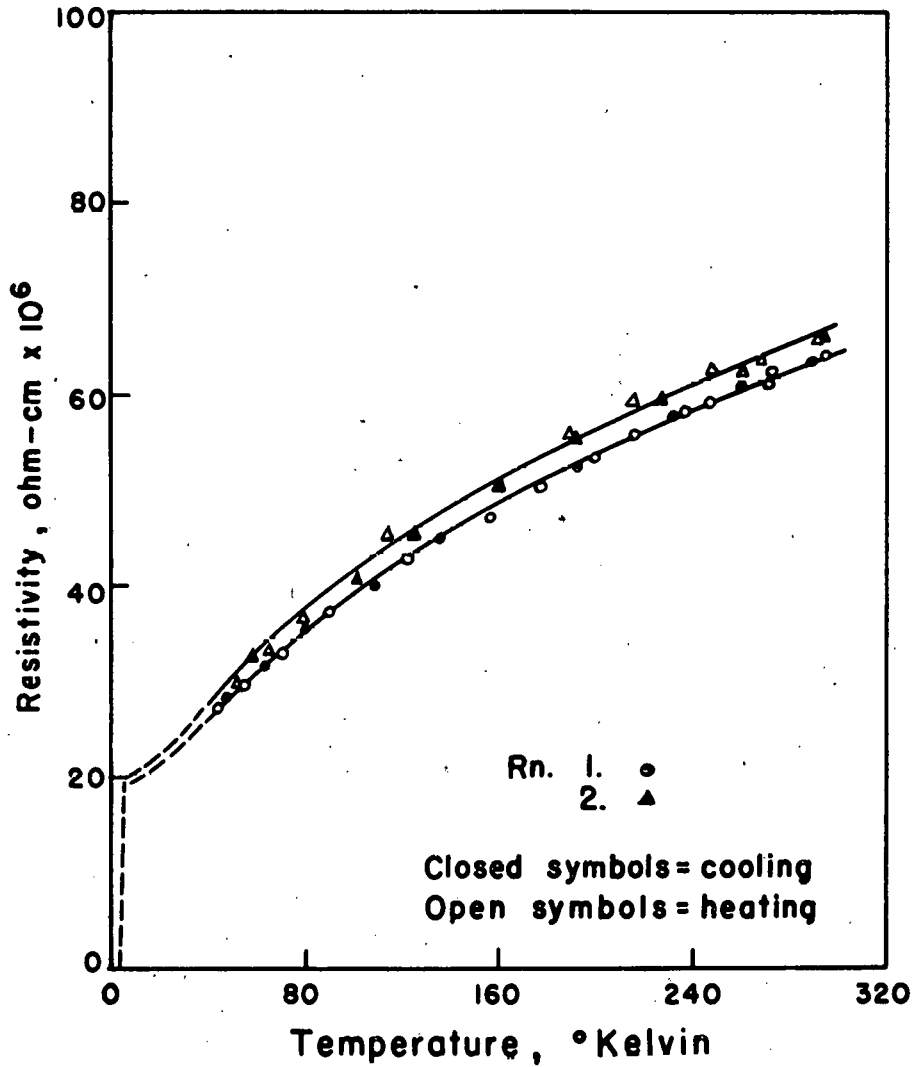   of temperature.

Fig. 2--Resistivity of Lanthanum II as a function
        of temperature.

Table 2

Constants for the Equation $[\rho] = aT^b$
for Lanthanum I and Lanthanum II

Sample	Run	$a \times 10^8$	b	Range of validity
La I	1	#		
	2	0.44	2.12	6 to 32°K.
	3	0.16	2.52	8 to 24
	4	0.99	1.98	8 to 32
La II	1	0.26	2.15	8 to 28
	2	0.27	2.18	8 to 28

#Data were not obtained at the transition temperature.

difference. La II might be expected to have a lower resis-
tivity than La I; first because it is of greater purity, and
second because there may have occurred, during the extrusion
of La II, an alignment of the crystals and consequently a
preferred direction for electron flow. That La I has the
lower residual resistivity, or would have were lanthanum not
a superconductor, is not surprising in view of the fact that
La I was annealed whereas La II was not. On the basis of
Matthiessen's rule, the large discrepancy between room-tem-
perature resistivities of the two samples, and the gradual
increase in resistivity of La I, it seems very unlikely that
the difference in impurity content has any significant effect.
Nor does it seem possible that the effect of extrusion is
large enough to cause the observed difference.

A third possible explanation of the difference in be-
havior of the two lies in the difference in structure of
the two specimens. La I was predominantly hexagonal after
the resistivity measurements; La II contained approximately
equal amounts of the hexagonal and cubic forms. It was
thought probable, because the room-temperature resistivity
of La I increased with successive measurements, that that
sample underwent at least a partial structural transition.
The variation of the resistivity at room temperature with
the length of time after the rod was first annealed is
shown in Figure 3. The sample, 123 days after the first
annealing, was predominantly hexagonal close-packed with
some oxide present. Since the resistivity did not continue
to increase after 80 to 90 days, it seems unlikely that
the change resulted from the gradual oxidation of the rod.
As has been mentioned, the small sample taken for the x-ray
analysis doubtless contained more oxide than did the rod.
In addition, the x-ray analysis was made a considerable
length of time after the last series of resistivity measure-
ments and therefore the x-ray sample would be expected to
contain a greater amount of oxide than did the rods. Further-
more, the resistivity of La II did not increase after the
second run, although both samples were kept under identical
conditions. Consequently, the most likely explanation of
the sudden increase in resistance of La I is that a struc-
tural change occurred, from the face-centered cubic to the
hexagonal close-packed form, with an accompanying increase
in resistivity. The third hypothesis, then, receives the
greatest support, both from the resistivity measurements
and from the x-ray analyses.

La I, at the time at which it was found to be predomi-
nantly hexagonal, had a resistivity of 100.5×10^{-6} ohm-cm.
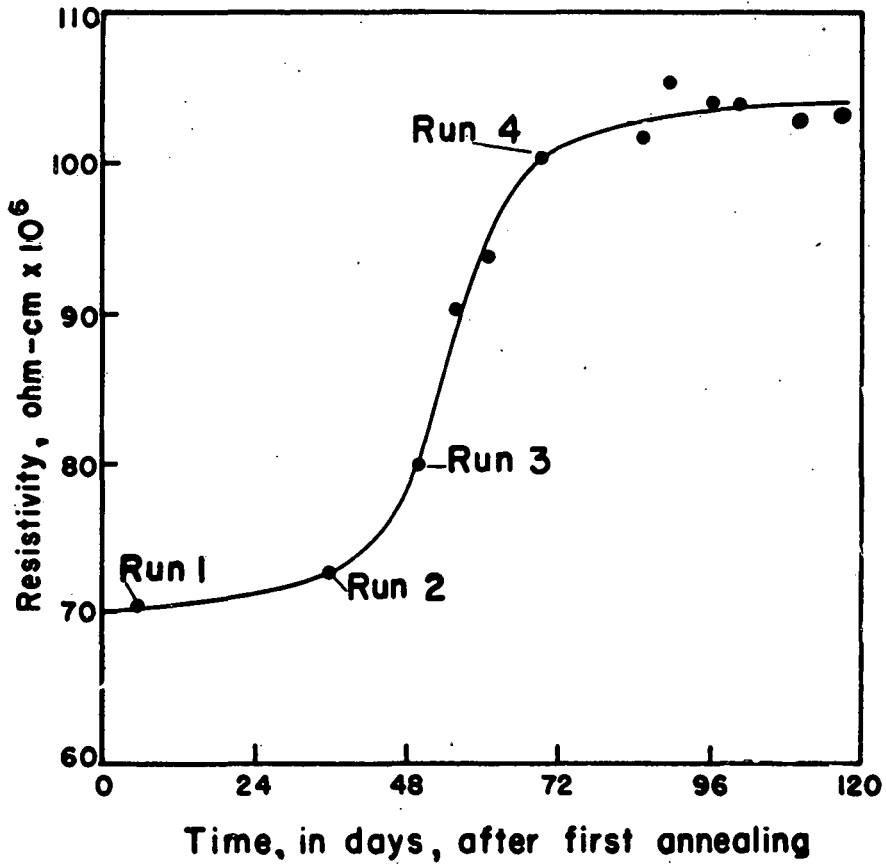at $300^\circ K$. At the same time, the resistivity of La II, which

Fig. 3--Resistivity at room temperature of Lanthanum I
as a function of length of time after first
annealing of the sample.

contained approximately equal amounts of the cubic and hex-
agonal forms, was 67.0 x 10^{-6} ohm-cm. The lowest value of
the resistivity of La I at 300°K. was 70.5 x 10^{-6} ohm-cm.;
that of La II was 64.5 x 10^{-6} ohm-cm. The difference between
these values and 57.6 x 10^{-6} ohm-cm., the value reported by
Bridgman (1927), is certainly not due to impurities. The low
value obtained by Bridgman may have been due to either an
alignment of the crystals during the extrusion process which
was more pronounced than that in La II or to a different crystal
structure. If the structure was different, then it must be
supposed that Bridgman's sample was predominently faced-centered
cubic, the form which according to the previous hypothesis
possesses the lower resistivity. It may be noted that up to
the present time the extrusion of hexagonal close-packed
lanthanum has not been reported.

It is known (Barrett, 1951) that cold work may not only
cause strain-induced transformations in pure metals but may
also inhibit spontaneous transformations by strain-hardening
the phase and inhibiting the movements of the atoms necessary
in spontaneous transformations. Thus it is possible that the
stable modification of lanthanum at room temperature is hex-
agonal close-packed, and that the cast sample underwent a
spontaneous transformation from the face-centered cubic to the
hexagonal close-packed structure while, at the same time, this
transformation was inhibited in the extruded specimen.

No anomaly was observed at 110°K. as was reported in the
magnetic susceptibility (Trombe, 1934).

4. The superconducting transition

The superconducting transition temperature, T_s, was taken
at the midpoint of the vertical portion of the resistivity
curve. The transition range, ΔT_s, was taken to be that over
which the vertical portion would have extended had there been
no rounding of the curve. The calculated temperatures and
transition ranges are given in Table 3. The data are shown
in Figures 4 and 5.

The transition temperatures for both samples are higher
than previously reported values, a fact which may be due to
the higher purity of the specimens used in the present study.
However, purer samples would be expected to exhibit a smaller
transition range. Such was not observed. In only one
case has such a large transition range been reported, that by
Ziegler, Floyd, and Young (1950), for specimen 2S. The spe-
cimen used by those workers was obtained from the same source
as the two used in the present work, but it is not clear
whether the heat treatment was the cause of the large transi-

Table 3

Calculated Superconducting Transition Temperatures
and Ranges of Lanthanum

Sample	Run	T_s, °K.	ΔT_s
La I	1	*	
	2	5.9	0.4
	3	6.0	0.3
	4	5.5	0.9
La II	1	5.8	0.3
	2	5.9	0.9

*The temperature of the transition was not observed.
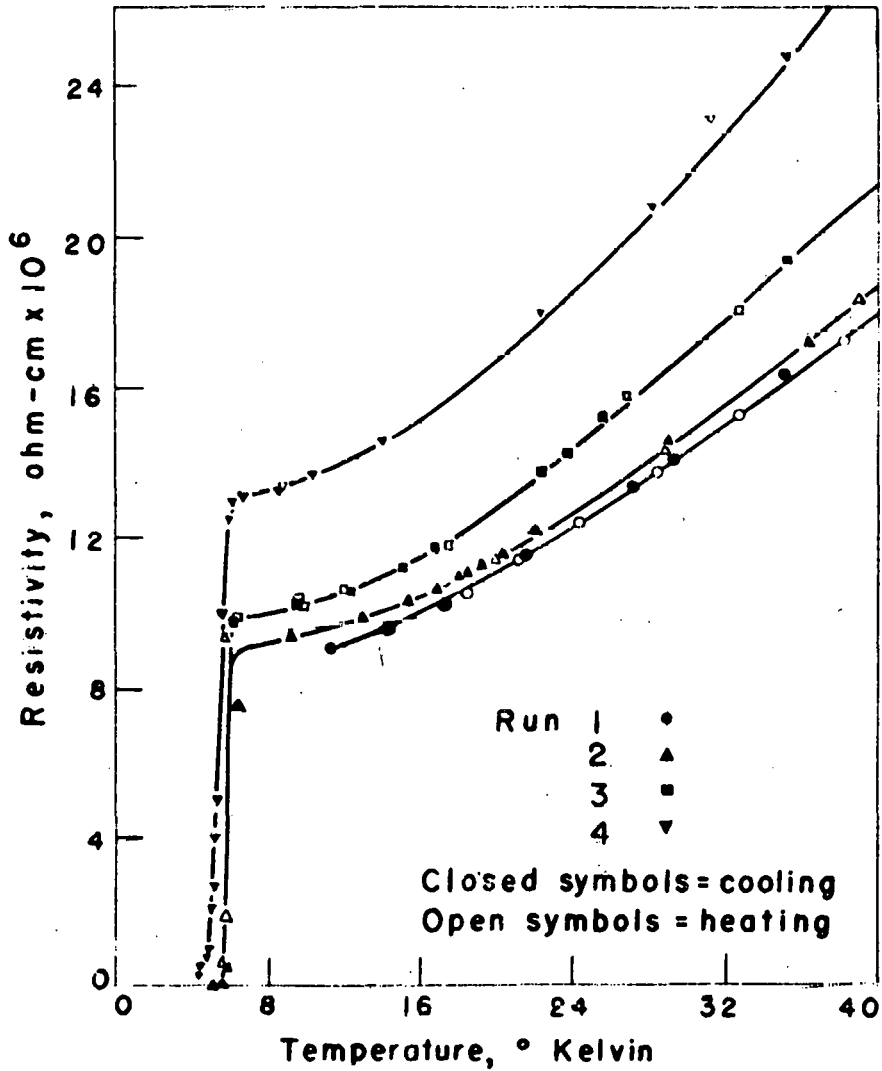
Fig. 4--Resistivity of Lanthanum I as a function
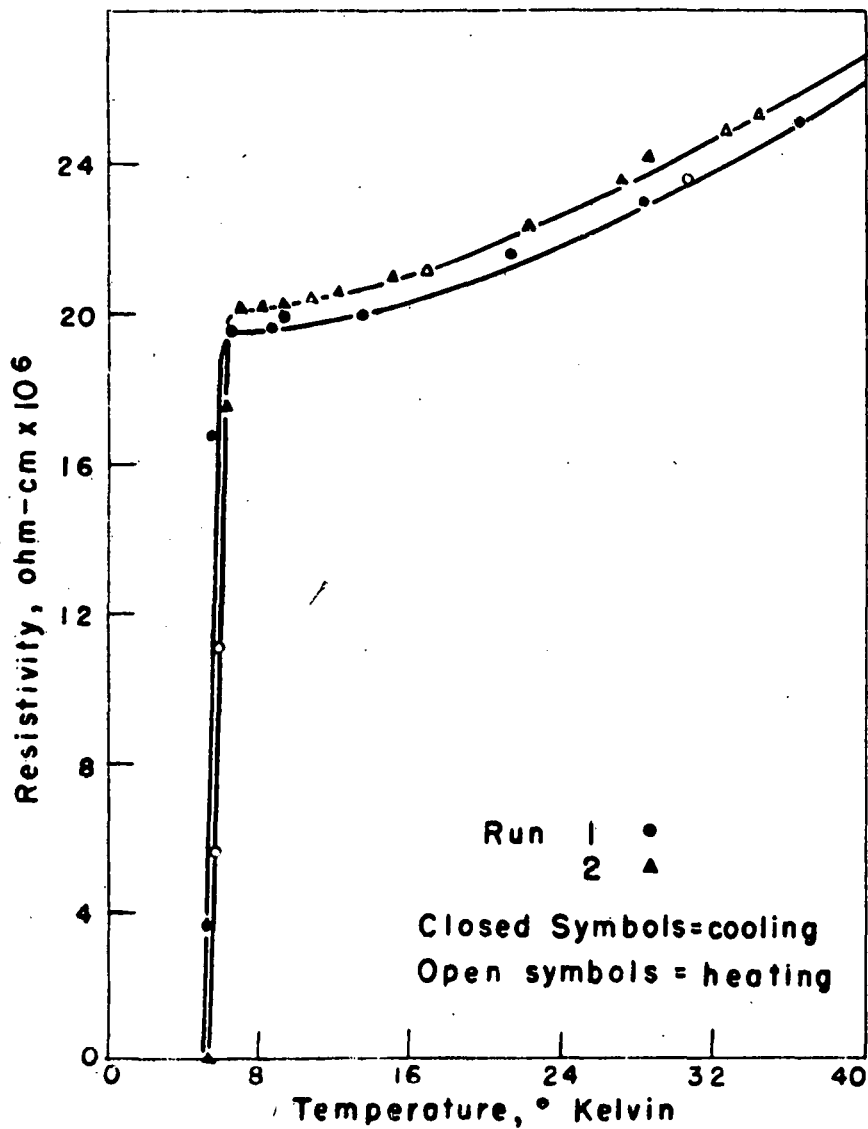of temperature below 40°K.

Fig. 5--Resistivity of Lanthanum II as a function
of temperature below 40°K.

tion range. Annealing did not increase the transition range of their other samples. In the present study, La I, which was annealed, exhibited approximately the same transition temperature and range as did La II, which was given no heat treatment other than that required by the extrusion process. The transition range of La I was not measured before the specimen was first annealed; however, as can be seen in Table 3, reannealing the rod after the second run did not increase the range. The rate of the transition, and hence the transition range, may be influenced by the grain size, as well as by imperfections in the crystal, but this in turn may be affected by heat treatment.

Ziegler, Floyd, and Young (1950) have suggested that both the cubic and the hexagonal forms of lanthanum are superconductors. Two samples, if of predominantly different crystal structures, might exhibit different superconducting transition temperatures. However, the transition temperature of a specimen containing a substantial proportion of each form would be the same as that of the form which showed the higher temperature of transition. If a difference in the transition temperatures of the two forms does exist, then on the basis of the previous assumption and the known crystal structures of the two samples studied, it must be concluded that the transition temperature observed in the present investigation is that of the hexagonal modification.

B. Cerium

1. History of the samples

Four samples of cerium were studied, all of which were annealed for 19 hours at 600°C., but cooled to room temperature in different periods of time. The method of preparation and properties of each are given in Table 4.

2. Crystal structure

No x-ray analysis of Ce I was obtained before the sample had completely oxidized. Ce II, after two series of measurements, contained mostly the face-centered cubic modification with a small amount of the hexagonal close-packed. After five thermal cycles, the lines due to the hexagonal structure were stronger, a fact which indicated that there was some increase in the amount of that form. Ce III, after annealing, contained only the cubic modifica-

Table 4

Method of Preparation and Properties of Cerium Samples

Sample	Method of Preparation	Length of cooling period hours	Iron content parts per million	Density g/cm^3
Ce I	Cast	3	700	
Ce II	Cast	1	2835	6.66
Ce III	Extruded	*	291	6.68
Ce IV	Extruded	24	291	6.68

*Sample was quenched in water at 25°C. immediately after annealing.

tion. After three series of measurements, lines due to the
hexagonal form were noted although the sample was still pre-
dominantly face-centered cubic. Both modifications were
present in Ce IV after annealing, the cubic form being pre-
dominant. After the third cycle, a considerable increase
in the amount of the hexagonal form was noted.

3. Resistivity

During cooling, the resistivity of all samples decreased
linearly from room temperature to approximately 120°K. The
data obtained above 40°K. are shown in Figures 6,7,8,9, and
13. All specimens showed a sudden decrease in resistivity
which began at a temperature between 100 and 120°K. and
which corresponded probably to the transition from the nor-
mal face-centered cubic structure to the more compact cubic
form. The corresponding increase in resistivity became ap-
parent, during heating, at approximately 170°K. and was com-
plete at approximately 220°K.

Ce I, cooled only to liquid nitrogen temperatures dur-
ing the first three sets of measurements, showed a smaller
decrease in resistivity each of these times, and effect si-
milar to that observed by Trombe and Foex (1944). The same
observation was made on the other cerium specimens only at
temperatures lower than that of liquid nitrogen. From the
x-ray analyses, it is apparent that there occurred a gradual
transition from the face-centered cubic form to the hexagonal
close-packed. An explanation of the smaller decrease in re-
sistivity at liquid nitrogen temperatures with successive
thermal cycles is afforded by the slow transition to the hex-
agonal structure and the probable inability of that form to
undergo a transition to the condensed cubic structure at
these temperatures.

At the end of the first set of measurements on each sam-
ple, the value of the room-temperature resistivity was high-
er than it had been at the beginning of the run. With the
exception of Ce II, the resistivity at room temperature of
all samples remained essentially constant after the first
run. That of Ce II increased further while the sample was
stored, but reached a constant value before the second series
of measurements was made. The cause of the increase is not
known. The greater reproducibility of the curves after the
first set of measurements may indicate that strains were or-
iginally present in the rods but were relieved during the
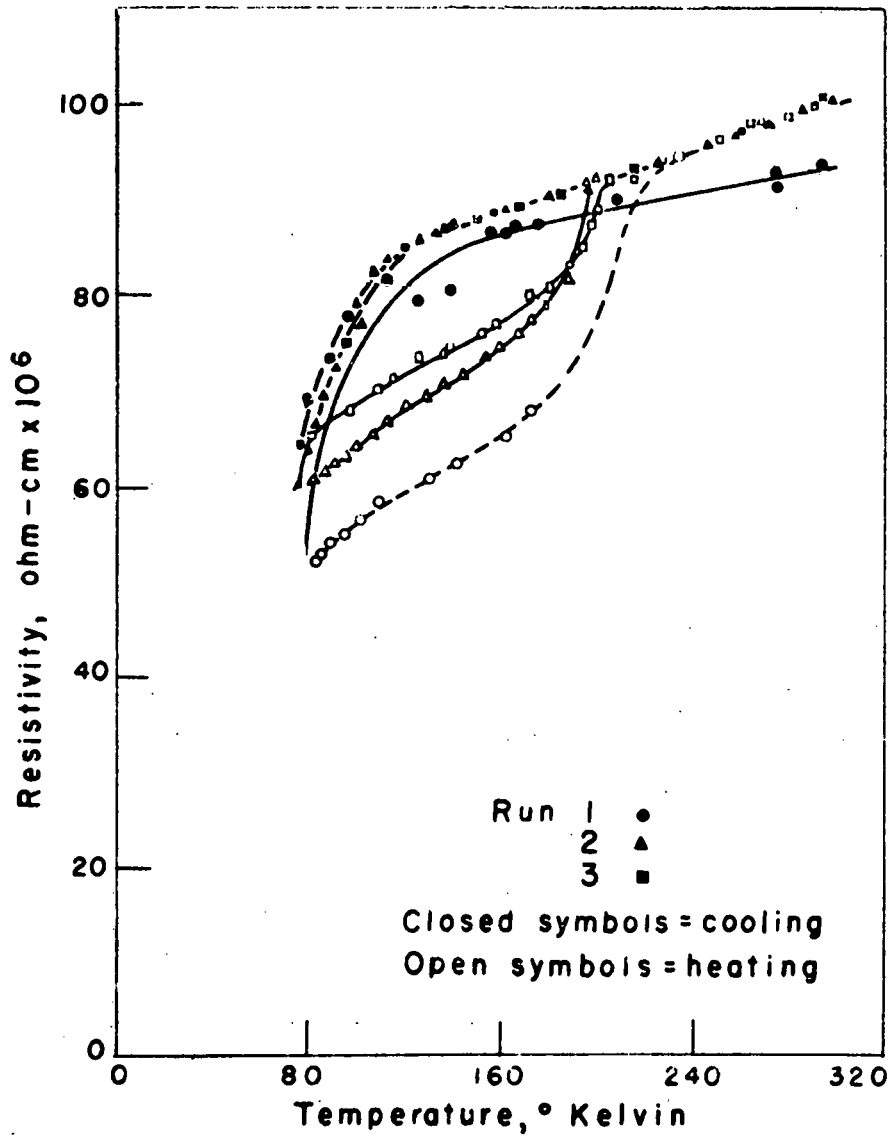first thermal cycle.

Fig. 6--Resistivity of Cerium I as a function of
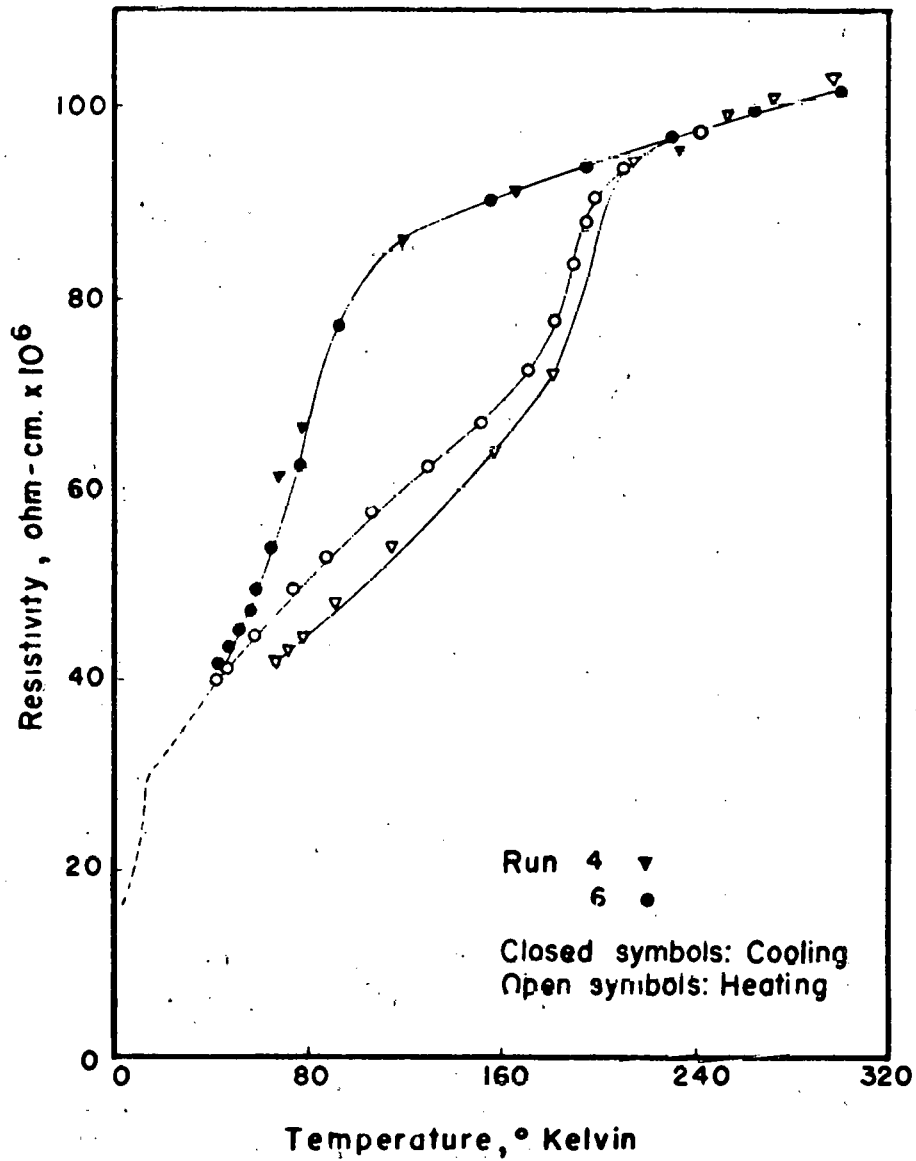temperature above 78°K.

Fig. 7--Resistivity of Cerium I as a function of
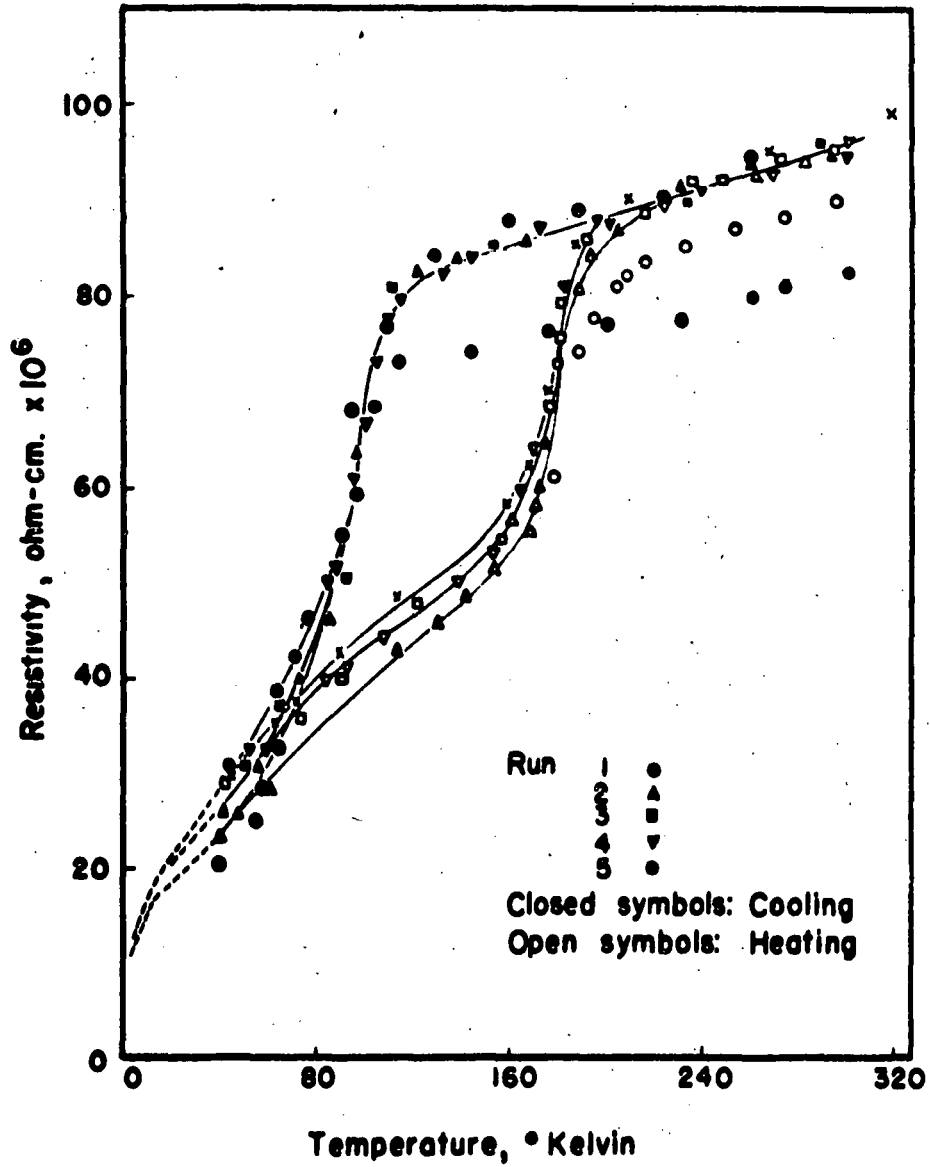   temperature.

Fig. 8--Resistivity of Cerium II as a function of
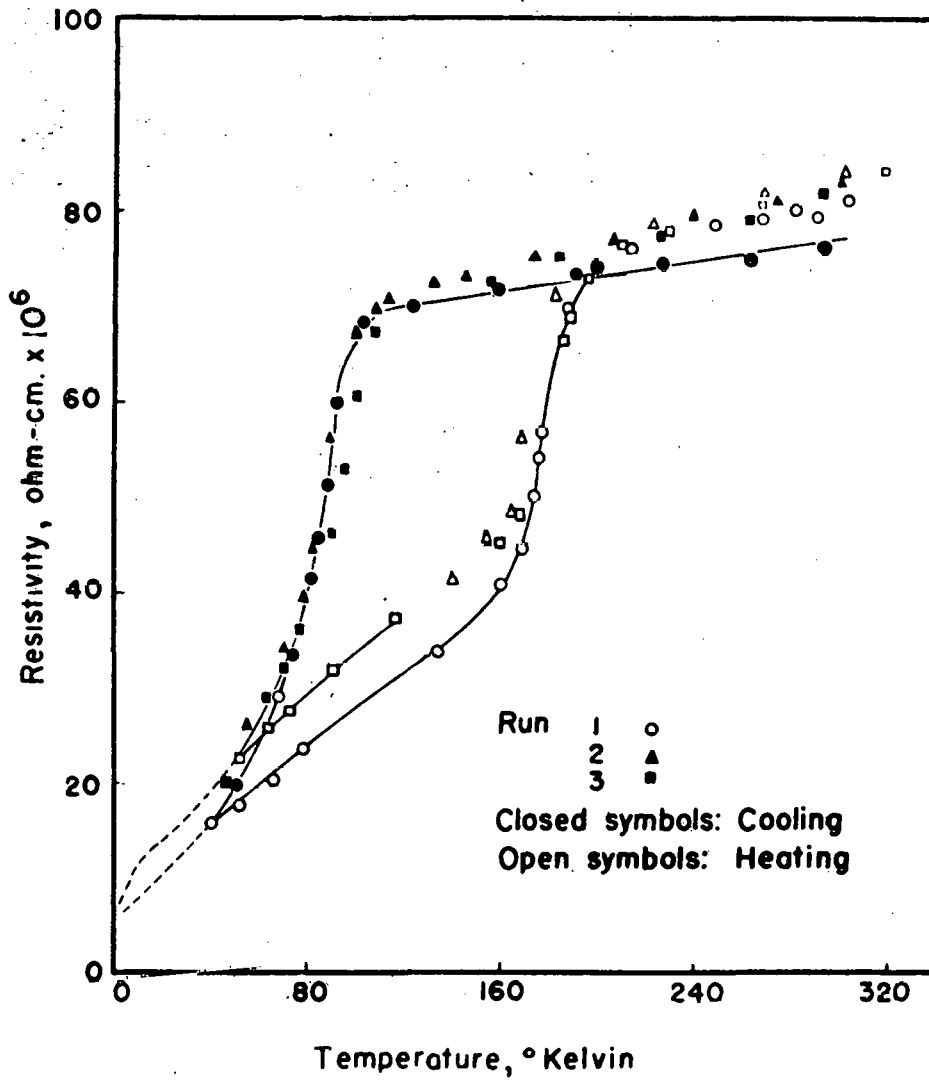   temperature.

Fig. 9--Resistivity of Cerium III as a function of
temperature.

A second anomalous decrease in resistivity occurred at a temperature between 11 and 14°K. The data are shown in Figures 10,11, and 12. The height of the small peaks in the curves was influenced, not by the rate of cooling as was the height of the peaks in the atomic heat curves of Parkinson, Simon, and Spedding (1951), but by the number of thermal cycles which the sample had undergone. Parkinson, Simon, and Spedding attributed the increase in the anomaly to an inhibition of the transition from the normal to the condensed cubic structure at the higher temperature caused by rapid cooling at the higher temperatures. However, it is not clear that the increase was not caused by successive thermal cycles alone. In the present investigation, the cooling rate was approximately the same for each series of measurements. That successive cycles effected more pronounced peaks in the curves as well as greater amounts of the hexagonal form suggests the possibility that the hexagonal crystals do transform into the condensed face-centered cubic structure at this lower temperature.

The rate of cooling from an annealing temperature to ordinary temperatures has been thought by several investigators to affect the behavior of cerium. The effect of the rate of cooling from the annealing temperature is evident from a comparison of Ce III with Ce IV. The specimens, having been cut from the same rod, were identical except for the length of the cooling period. Ce III was quenched in water at 25°C. immediately after annealing; the x-ray analysis did not indicate the presence of any hexagonal crystals. Ce IV was cooled in a period of 24 hours and contained a considerable amount of the hexagonal modification. After the third series of measurements the proportion of the hexagonal form had increased only slightly in Ce III but considerably in Ce IV. A pronounced difference appears in the resistivity curves which are shown in Figures 12 and 13. Data obtained from the first two series of measurements of Ce IV are omitted because of incompleteness. However, these data gave no indication of inconsistencies. The resistance of Ce IV decreased more slowly at liquid nitrogen temperatures and correspondingly, a sharper knee in the curve appeared at approximately 12°K. Again, the curves of Ce III in Figure 12 show the increase in the low-temperature anomaly which accompanies the increase in the amount of the hexagonal structure. The results here obtained uphold the theory of Trombe·and Foex (1943 and 1944) that slow cooling after annealing and repeated thermal cycles between room temperature and low temperatures invoke a gradual transition from the γ [cubic] to the β [hexagonal] modification. However, in the present investigation, the quenched speci-
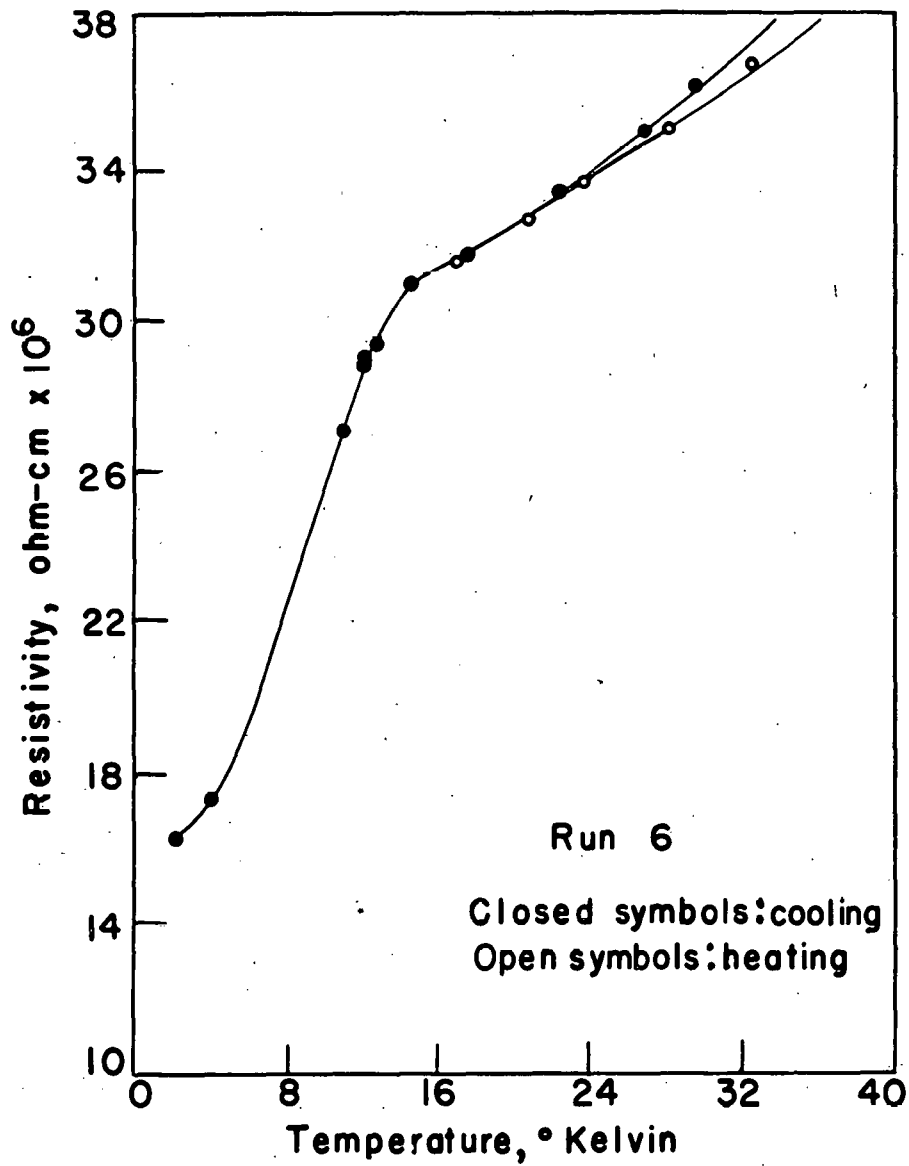
Fig. 10--Resistivity of Cerium I as a function of
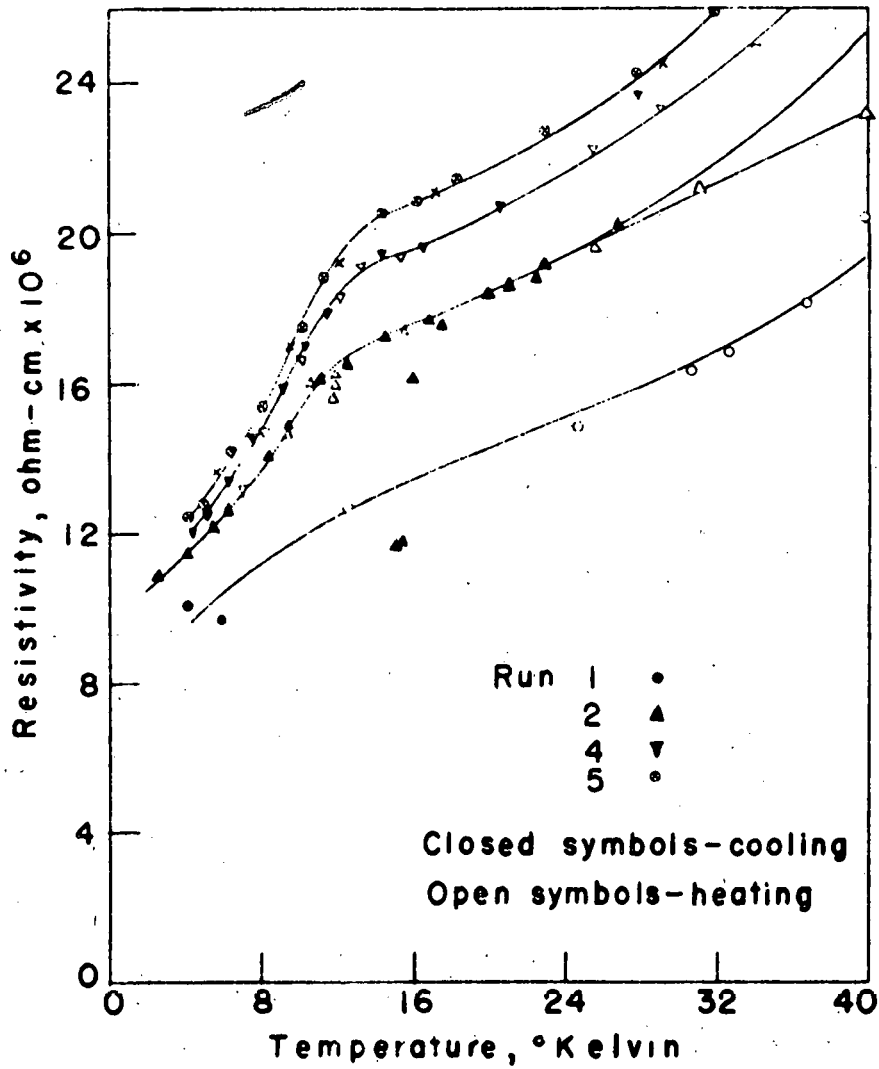temperature below 40°K.

Fig. 11--Resistivity of Cerium II as a function of
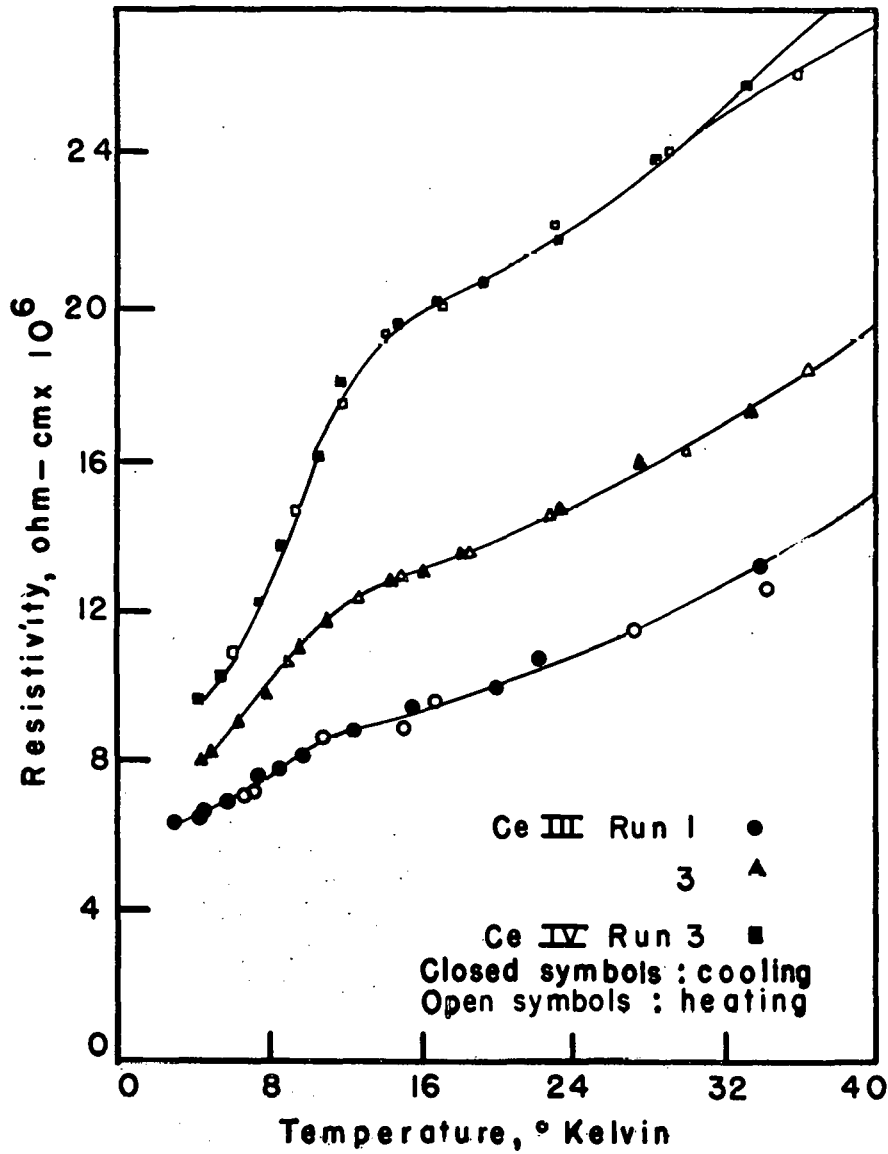temperature below 40°K.

Fig. 12--Resistivity of Cerium III and Corium IV as
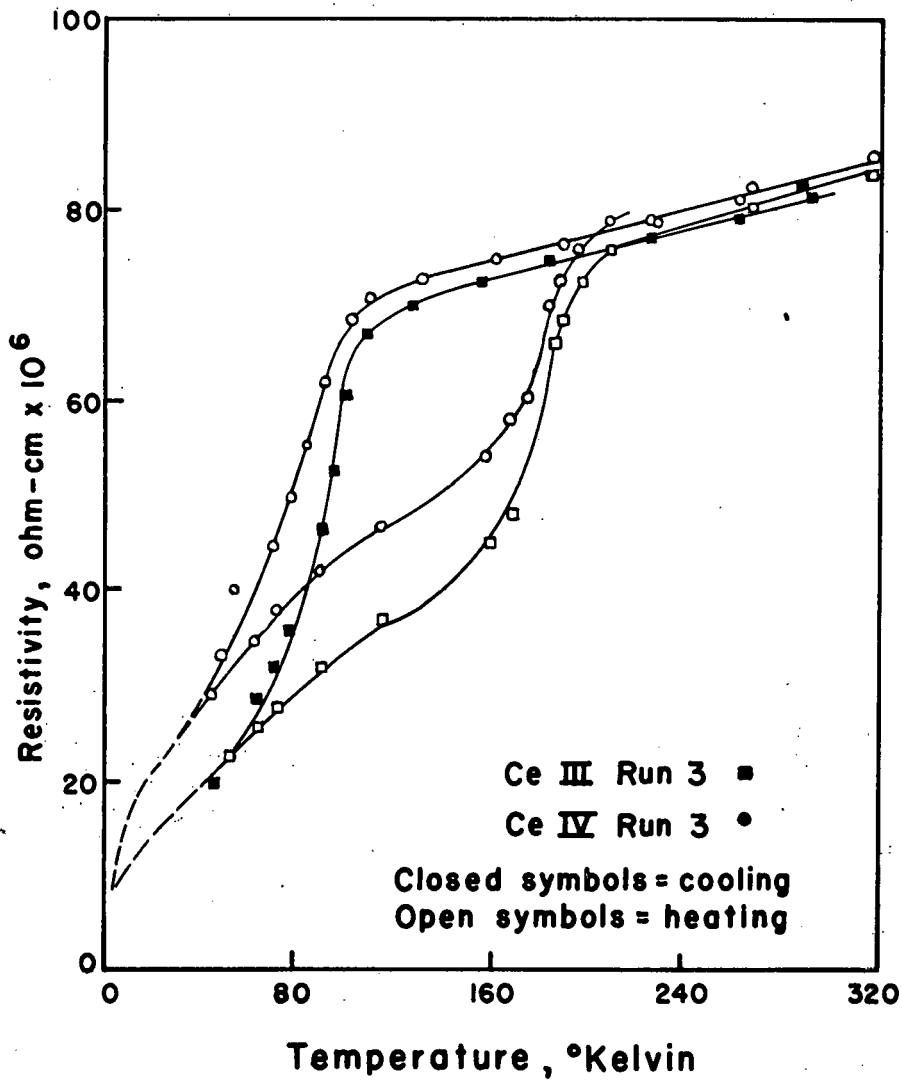a function of temperature below 40°K.

Fig. 13--Resistivity of Cerium III and Cerium IV
as a function of temperature.

men did not exhibit perfectly reproducible behavior, but
transformed also, although at a much slower rate. The in-
ability of Schuch and Sturdivant (1950) to observe the trans-
ition with a slowly cooled face-centered cubic sample remains
unexplained. It may also be noted from the high value of
R/R_0 reported by McLennan, Allen, and Wilhelm (1930) and by
de Haas and Voogd (1932) that the specimens used by these
workers apparently did not undergo the transition.

The resistivity data together with the x-ray evidence
corroborate the theory that the decrease in resistivity that
occurs at liquid nitrogen temperatures is due to a transi-
tion from the normal face-centered cubic form to the con-
densed cubic form, that the smaller decrease that occurs with
successive thermal cycles is due to the formation of the hex-
agonal structure and the inability of that structure to under-
go a transition to the condensed cubic form, and that the low-
temperature anomaly is due to a transition from the hexagon-
al close-packed to the condensed face-centered cubic struc-
ture, or, possibly, to a condensed hexagonal structure.

C. Praseodymium

1. History of the sample and crystal structure

The praseodymium sample was cast, annealed before the
first resistivity measurements and again before the third.
The density was 6.59 g/cm^3; the iron content, 315 parts per
million. An x-ray taken after the third series of measure-
ments indicated that the sample was 75 per cent hexagonal
close-packed with a = 3.64 and c = 5.89 A^o., and 25 per cent
face-centered cubic with a = 5.11 A^o. Some oxide was pre-
sent.

2. Resistivity

The data obtained are shown in Figures 14 and 15. Above
160°K. the curves are nearly linear in general agreement
with theory. The values of a and b in the equation
$[\rho] = a T^b$ are given in Table 5. As in the case of lantha-
num, the values of b are much lower than Bloch's theoreti-
cal value of 5. The slight increase in resistivity after the
rod had been annealed is greater than the experimental er-
ror and may be due to the relief of strains within the rod.
The room-temperature resistivity did not continue to increase
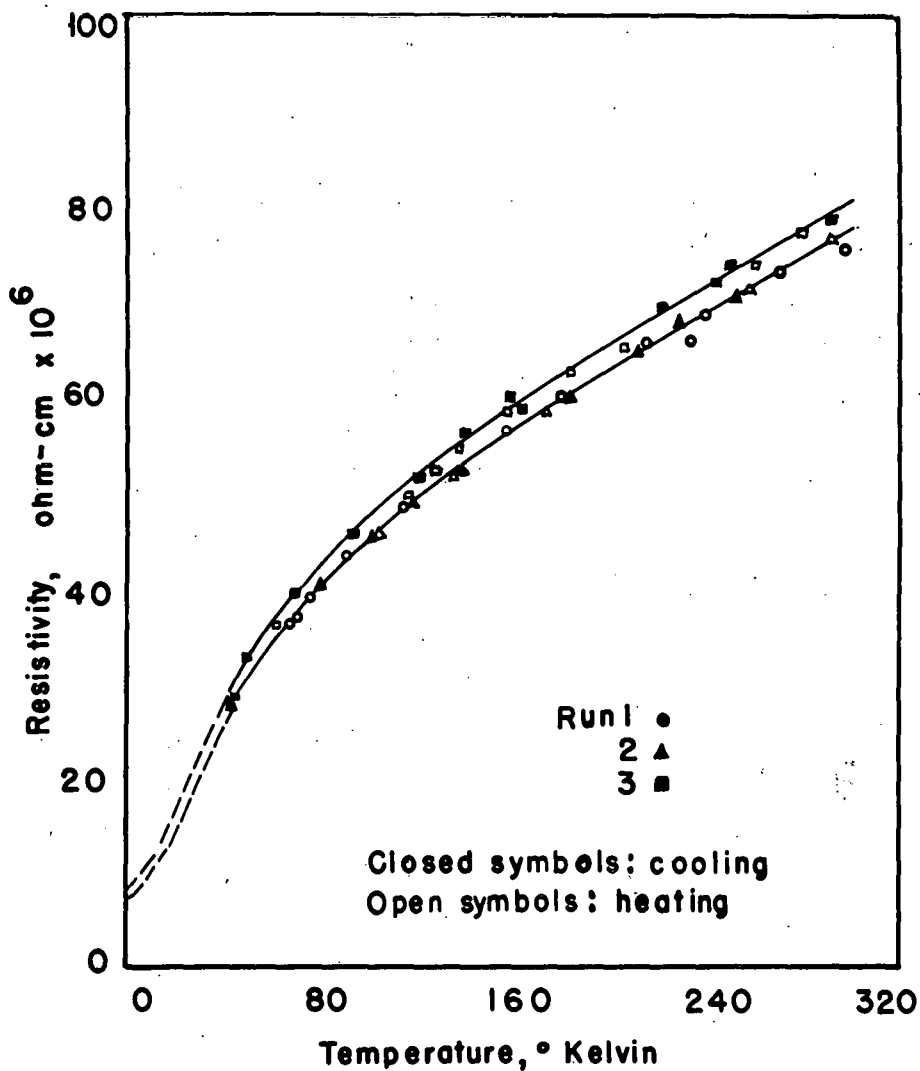after the third series of measurements.

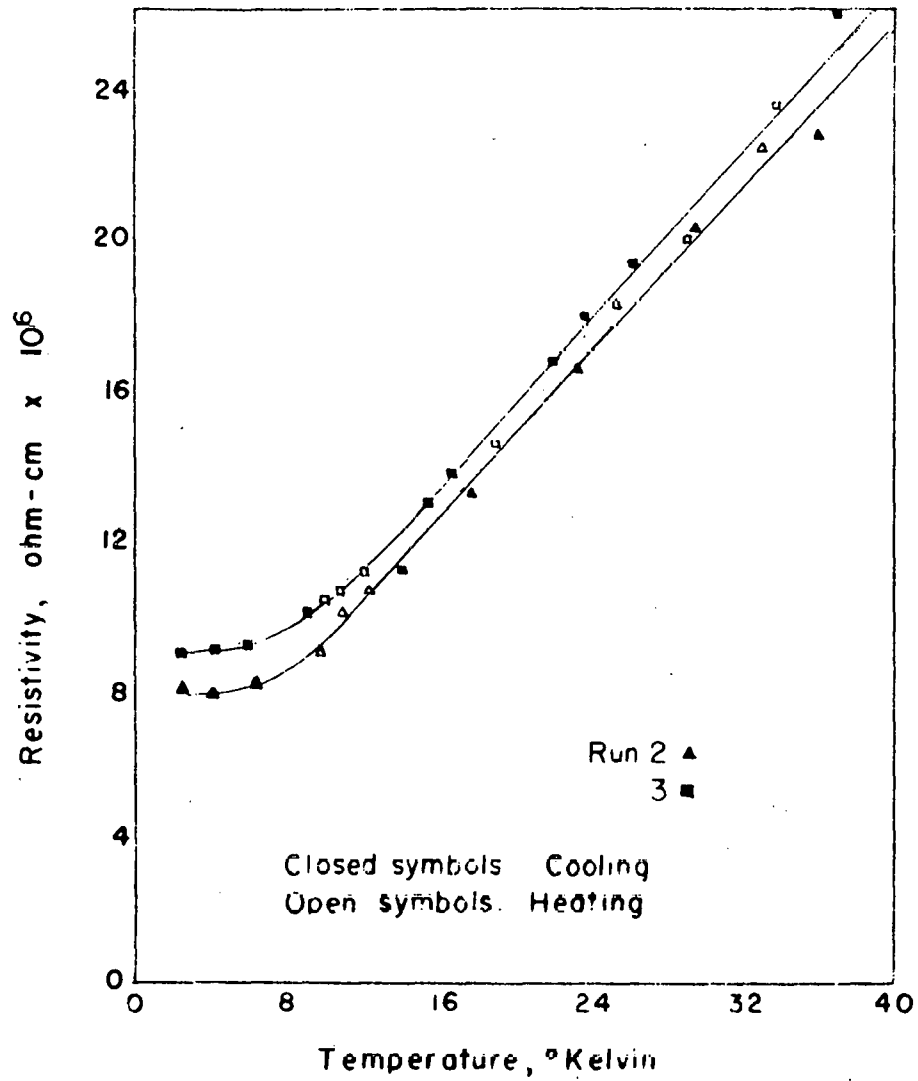Fig. 14--Resistivity of Praseodymium I as a function
of temperature.

Fig. 15--Resistivity of Praseodymium I as a function
of temperature below 40°K.

Table 5

Constants for the Equation $[\rho] = aT^b$ - for Praseodymium I

Run	a x 10^8	b	Range of validity
2	2.19	1.82	2 to 12°K.
3	4.96	1.00	2 to 6
3	0.10	3.12	6 to 12

A comparison of the behavior of praseodymium with that of hexagonal lanthanum (La I, Run 4, Figure 1) indicates that the resistivity of the former was considerably lower throughout most of the temperature range. Since both samples were of the same crystal structure, the lower resistivity of praseodymium suggests that the smaller ion size has the effect of increasing the electronic conduction.

The slope of the low-temperature portion of the curve was greater than that of lanthanum or neodymium although an anomaly in the latter curve makes a fair comparison difficult. The greater slope in the praseodymium curve is an effect which is similar to that observed by Parkinson, Simon, and Spedding (1951) in the atomic heat curves and remains unexplained.

That the room-temperature resistivity was somewhat higher than 69 x 10^{-6} ohm-cm., the value reported by Bridgman (1927) for an extruded wire, suggests again the possibility that the extrusion process lowers the resistance by affecting an alignment of the crystals.

D. Neodymium

1. History of the sample and crystal structure

The neodymium sample was cast, annealed immediately after casting and again after the second series of measurements. Its density was 6.86 g/cm^3; the iron content, 178 parts per million. An x-ray taken after the last resistivity measurements showed only the hexagonal close-packed structure, with a = 3.62 and c = 5.76 A°., and a small amount of the oxide to be present.

2. Resistivity

Figures 16 and 17 show the data obtained. The behavior above 24°K. was that of a normal metal and was the most reproducible of the rare earths studied. Again, the linear decrease of resistivity with temperature at the higher temperatures agrees with theoretical prediction.

Below 24°K. an anomaly appeared which was centered at approximately 12°K. and which became more evident with successive thermal cycles. A splitting of the lowest energy level of the ion by the field of its neighbors and a consequent redistribution of the electrons, suggested by Parkinson, Simon, and Spedding (1951), might well result in a modification of the expected resistivity pattern. Since neodymium is not known to exist in the face-centered cubic form, it is apparent that the cause of the increase in the low-temperature anomaly differs from that supposed in the case of cerium.

A comparison of the resistivities of the three hexagonal close-packed elements (La I, Run 4, Figure 1; Pr I, Figure 14; and Nd I, Figure 16) shows again the decrease in the resistivity effected by the decrease in the ion size. The abnormal negative derivative of the slope of the low-temperature end of the neodymium curves makes it highly desirable to pursue the investigation at temperatures lower than 2°K.

VI. SUMMARY

1. Evidence is presented to support the hypothesis that the face-centered cubic form of lanthanum possesses a much lower resistivity at ordinary temperatures than does the hexagonal close-packed form. The possibility is suggested that the cubic crystals may undergo a slow spontaneous transformation into the hexagonal modification at these temperatures, the hexagonal form being the more stable of the two. It is possible that the method of preparation of the samples affects their resistance, and positive conclusions drawn from a comparison of La I with La II are therefore likely to be in error. Nevertheless, it is probable that the room-temperature resistivity of face-centered cubic lanthanum is less than 70×10^{-6} ohm-cm. and that of hexagonal close-packed lanthanum, approximately 100×10^{-6} ohm-cm.
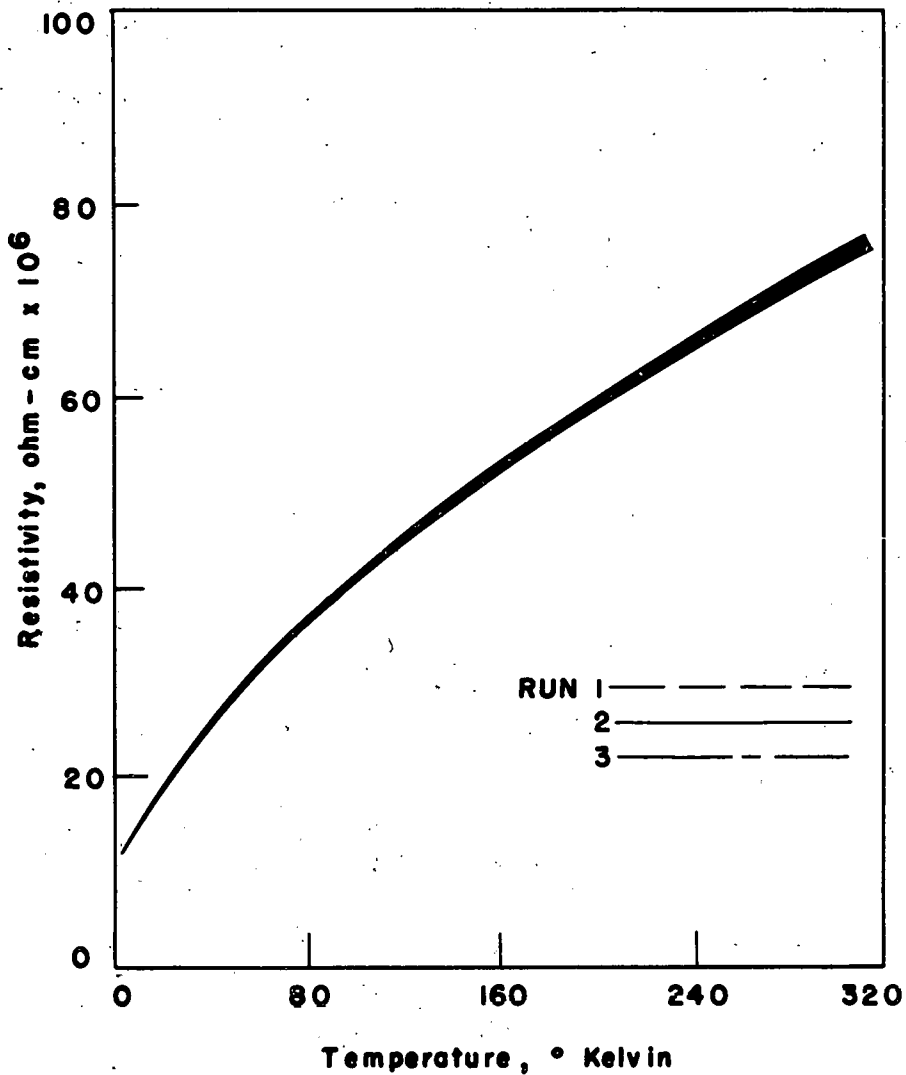
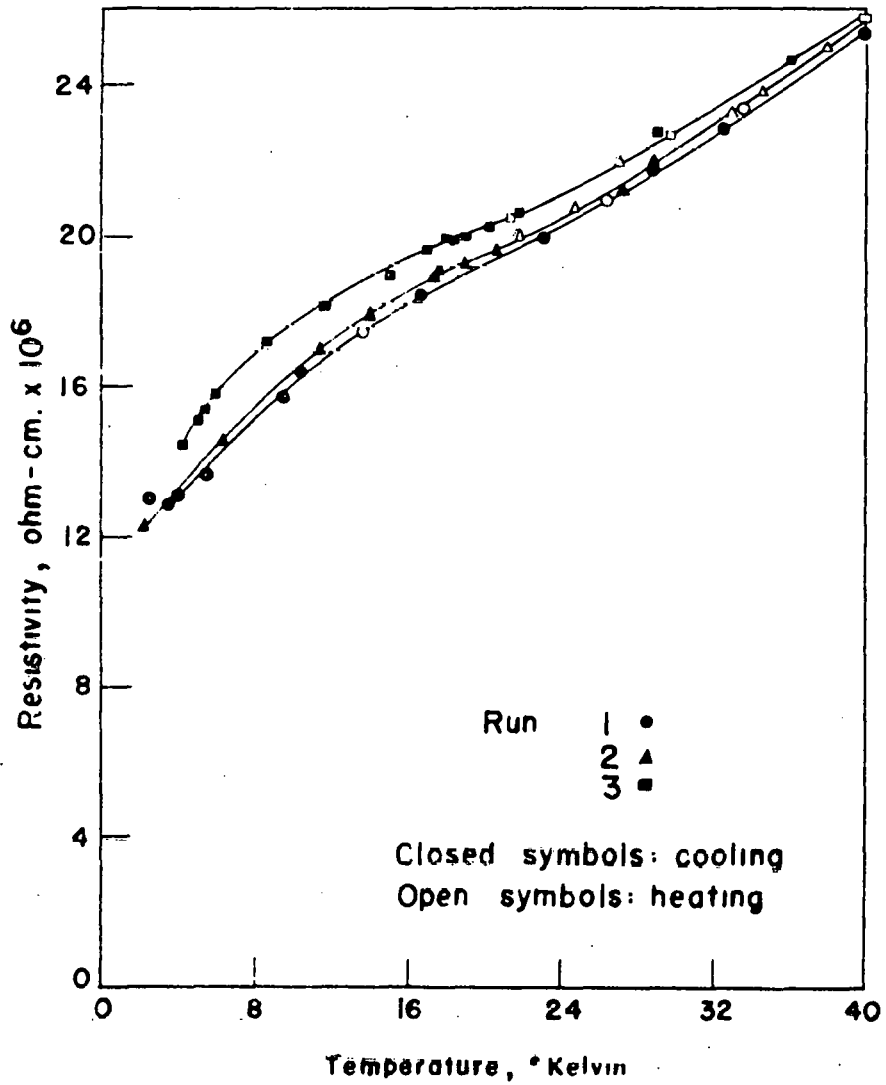Fig. 16--Resistivity of Neodymium I as a function
of temperature.

Fig. 17--Resistivity of Neodymium I as a function
of temperature below 40°K.

2. The equation $[\rho] = aT^b$ was found to be valid for the resistivity of lanthanum in the approximate temperature range from 8 to 28°K. The average calculated value of b was 2.19.

3. An average superconducting transition temperature for lanthanum was found to be 5.8°K. This is probably that temperature at which the hexagonal close-packed form loses its resistance. The possibility exists that face-centered cubic lanthanum becomes superconducting at a lower temperature. The cause of the large transition range, 0.3 to 0.9 degree, is unknown. The effect of annealing was not determined in this investigation.

4. Evidence is presented to show that the transition in cerium from the normal face-centered cubic structure to the condensed face-centered cubic form at liquid nitrogen temperature is accompanied by a large decrease in resistivity.

5. Further evidence indicates that the face-centered cubic crystals of cerium may gradually transform into the hexagonal modification and that the hexagonal form also shifts to the condensed cubic structure (or to a condensed hexagonal close-packed structure) at a temperature between 11 and 14°K. The rate of the transition from the face-centered cubic structure to the hexagonal close-packed is shown to be dependent upon the rate of cooling from the annealing temperature to room temperature.

6. The resistivity of praseodymium was found to follow the equation $[\rho] = aT^b$ at low temperatures.

7. The small low-temperature anomaly in the resistivity of neodymium, centered at approximately 12°K., is possibly explained by a splitting of the lowest energy level of the ion by the field of its neighbors and a consequent redistribution of the atoms among these states. The cause of the increase in the anomaly with successive thermal cycles may be the result of annealing in the process of measuring the resistivity.

8. A decrease in resistivity was found to be correlated with an increase in atomic number.

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