interaction constant with J is not excluded by our experiments as an explanation for the discrepancy between the electric and magnetic resonance results. Unfortunately, with the inhomogeneous fields available in our apparatus it was not possible to examine spectra for J greater than 2.

It will be noted that in Table II the calculated and observed line positions in all but two cases agree within experimental error. Thus, a single $\mathbf{I}\cdot\mathbf{J}$ interaction, the F interaction, explains the data rather well. However, there are indications that there may be systematic differences between the observed and calculated line positions; e.g., for $J=1$ the observed line positions are all higher than the calculated positions. If such systematic differences do in fact exist, they might be expected to be caused by the interactions involving the Li nucleus. In order to determine the effect of these interactions it would be necessary, in general, to solve sixth degree equations, a rather hopeless procedure with the present information about the Li interactions. Calculations at zero field, however, showed that shifts in line positions of several kc/sec might be produced by the Li interactions. Thus, though it is not possible with the present resolution of the apparatus to resolve the fine structure produced by the Li interactions, it might be possible nevertheless to get some information about these interactions from the line positions observed near zero field. Unfortunately, such a program is not feasible at present because of the lack of information about the relative amplitudes of the different spatial components of the radiofrequency voltage.

The authors are indebted to Dr. R. G. Luce for his help in the construction of the mass spectrometer used in these experiments. The help of Mr. R. Braunstein and Mr. D. T. F. Marple in the laboratory is gratefully acknowledged.

PHYSICAL REVIEW VOLUME 88, NUMBER 5 DECEMBER 1, 1952

The Resistivity of Lanthanum, Cerium, Praseodymium, and Neodymium at Low Temperatures*

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(Received August 15, 1952)

The electrical resistivity of lanthanum, cerium, praseodymium, and neodymium metals from room temperature to 2.2°K is presented. The h.c.p. modification of lanthanum is found to possess a higher resistivity than the f.c.c. The mean of the observed superconducting transition temperatures for lanthanum is 5.8°K. Anomalies in the resistivity of cerium which occur at liquid nitrogen temperatures and between 11 and 14° K are discussed in connection with the crystal structure. An anomaly in the resistivity of neodymium occurs at approximately 12°K.

I. 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, electrical, 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 and purity bear the greatest significance. In this preliminary study an attempt has been made to ascertain how these factors affect the electrical resistivity.

II. EXPERIMENTAL METHOD

A Collins Helium Cryostat with the samples and thermometers mounted just above the bottom of the experimental chamber was used for the experiments. The length of time required to cool the apparatus averaged $7\frac{1}{2}$ hours; heating occurred over an average period of 45 hours.

Temperatures between 300 and 15°K were determined by a four-lead standard platinum resistance thermometer, No. 718171, made by Leeds and Northrup Company and calibrated down to 10°K by the National Bureau of Standards. Below 15°K a four-lead constantan resistance thermometer was used. The thermometer winding consisted of No. 30 B. and S. cotton-covered wire, wound loosely, in order to be strain-free, and non-inductively on Bakelite micarta tubing. The constantan thermometer was calibrated between 25 and 10°K against the platinum thermometer, at 4.2 and at 2.2°K by immersion in liquid helium at atmospheric pressure and at the λ-point. Temperatures below 15°K

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* Contribution No. 203 from the Institute for Atomic Research and Department of Physics, Iowa State College, Ames, Iowa. Work was performed in the Ames Laboratory of the AEC.

† Now at Chalk River, Ontario, Canada. The material reported here appears in the first author's thesis presented to the Graduate Faculty of the Iowa State College in partial fulfillment of the requirements for the Doctor of Philosophy degree.

TABLE I. Method of preparation and properties of specimens.

Sample	Method of preparation	Runs preceded[a] by annealing	Length of cooling period, hours	Iron content, parts, per million	Density, g/cm^3	Structure[b]
La I	Cast	No. 1, No. 3	3, 3	4200	6.08	After Run 4: two-thirds h.c.p., one-third f.c.c.
La II	Extruded	No annealing		85.5	5.98	After Run 2: one-half h.c.p., one-half f.c.c.
Ce I	Cast	No. 1	3	700	Not obtained	Not obtained
Ce II	Cast	No. 1	1	2835	6.66	After Run 2: predominantly f.c.c., small amount h.c.p. After Run 5: some increase in amount of h.c.p.
Ce III	Extruded	No. 1	Quenched in water at 25°C	291	6.68	Before Run 1: entirely f.c.c. After Run 3: small amount h.c.p.
Ce IV	Extruded	No. 1	24	291	6.68	Before Run 1: predominantly f.c.c., some h.c.p. After Run 3: considerable increase in amount of h.c.p.
Pr I	Cast	No. 1, No. 3	3, 1	315	6.59	After Run 3: three-fourths h.c.p., one-fourth f.c.c.
Nd I	Cast	No. 1, No. 3	3, 1	178	6.86	After Run 3: entirely h.c.p.

[a] Samples were annealed for 19 hours at 600°C.

[b] The relative amounts of the two crystal forms present in the samples was determined by x-rays on samples cut from the ends of the rods and then filed into the form of needles. As a consequence these results are only qualitative.

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 Rubicon Mueller temperature bridge. Thermometer readings were taken both before and after the measurements of the potential 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 at least the nearest degree and below 40°K temperatures were read to the nearest one-tenth of a degree.

The metals used were prepared by a bomb reduction technique.[1] 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 1-cm diameter magnesium oxide tube, the process being done in a vacuum. The extruded rods were 6.4 mm in diameter. All rods were turned on a lathe to approximately 3.6 mm in diameter and cut to 5 cm in length. They were generally stored in a helium atmosphere in soft glass tubes, although for a short time they were kept under mineral oil. Properties of the specimens are shown in Table I.

Spectrographic analyses showed that all specimens contained less than 1-percent magnesium, less than 0.025 percent calcium, and less than 0.01 percent other rare earths. These values represent the limits of detectability spectrographically. 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 0.2 mm in diameter.

The resistivity was determined by the standard method of comparing the potential drop across the sample to that across a standard resistance connected in series with it. 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. Three 6-volt storage batteries, connected in parallel in order to insure a more uniform current, were used for the supply. A current of approxi-

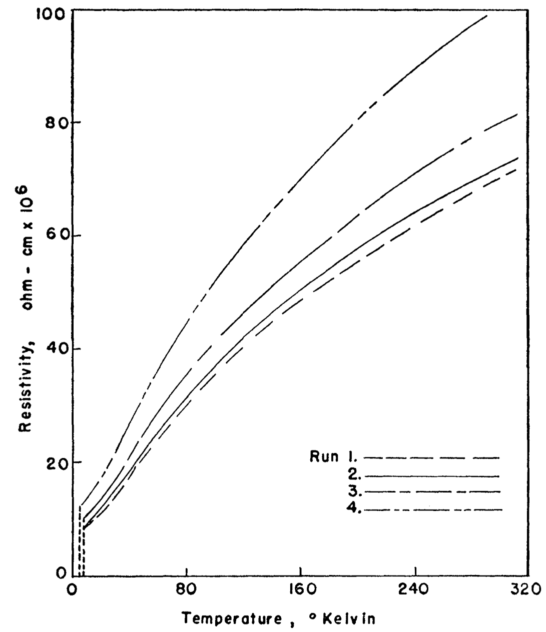

FIG. 1. Resistivity of lanthanum I as a function of temperature.

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[1] Spedding, Wilhelm, Keller, Ahmann, Daane, Hach, and Erickson, Ind. Eng. Chem. 44, 553 (1952).

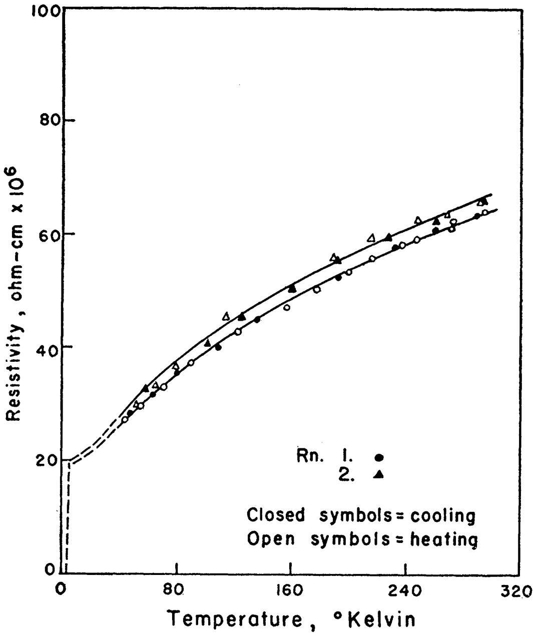

FIG. 2. Resistivity of lanthanum II as a function of temperature.

mately ½ ampere was sufficient to give a measurable potential drop across the samples at all temperatures. Potential drops were measured on a Rubicon Type B potentiometer.

The sample holder contained clamps for three rods and space for the two thermometers. Selector switches permitted any one sample to be connected into the circuit. The thermometers, placed as close together as possible, were approximately one cm from two of the samples and three cm from the third. Current connections to the samples were rigid brass wedges against which the rods were forced by small brass springs under tension. The ends of the springs were filed to wedge shapes and were used for potential connections. Before the rods were mounted in the holder, the oxide coating was removed with fine sandpaper and crocus cloth. The separation of the potential leads was marked by dividers and estimated to the nearest 0.1 mm. The mean of three readings, with a probable error never greater than 0.1 mm, was used in the calculations. In these preliminary measurements no correction was made for the change in length due to temperature variation.

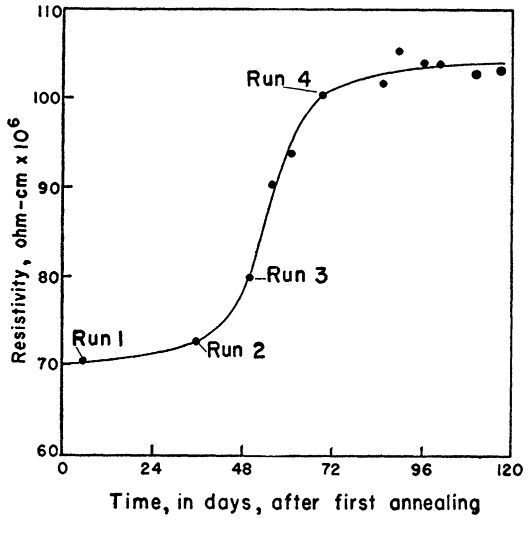

FIG. 3. Resistivity at room temperature of lanthanum I as a function of length of time after first annealing of the sample.

III. RESULTS AND CONCLUSIONS

A. Lanthanum

There is a marked difference in the behavior of the two specimens of lanthanum as can be seen in Figs. 1 and 2. After La sample I was first annealed, its resistivity at room temperature increased over a period of 90 days following which it remained essentially constant. This is shown in Fig. 3 where the room temperature resistivity is given as a function of time in days. Data on the resistivity as a function of temperature were taken during the time that the room temperature resistivity was changing slowly, and this accounts for the spread in the curves of Fig. 1. The points at which the temperature runs were made are indicated on Fig. 3. An x-ray analysis, obtained 123 days after the first annealing, showed the sample (La I) to be predominantly hexagonal close-packed (h.c.p.).

TABLE II. Calculated superconducting transition temperatures and ranges of lanthanum.

Sample	Run	T_s, °K	ΔT_s
La I	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 resistivity of La sample II increased only slightly from run 1 to run 2 (see Fig. 2). The resistivity did not change appreciably thereafter with time. La II was found to contain approximately equal amounts of the hexagonal close-packed (h.c.p.) and the face-centered cubic (f.c.c.) modifications. The results suggest the possibility that the stable modification of lanthanum at room temperature is h.c.p. and that the cast sample, La I, underwent a spontaneous transformation from the f.c.c. to the h.c.p. structure with an accompanying increase in resistivity while, at the same time, this transformation was inhibited in the extruded specimen, probably by the work done during extrusion.

Previous measurements of the superconducting transition of lanthanum have led to considerable disagreement. Mendelssohn and Daunt[2] observed the transition by magnetic methods at 4.71°K; Shoenberg[3] using the

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[2] K. Mendelssohn and J. G. Daunt, Nature **139**, 473 (1937).

[3] D. Shoenberg, Proc. Cambridge Phil. Soc. **33**, 577 (1937).

magnetic method observed it at 4.2°K; Ziegler[4] found by the magnetic method for two samples 4.85±0.15 and 4.45±0.10°K, with a transition range of less than 0.1 degree. Ziegler, Floyd, and Young[5] found by the magnetic method for various specimens transition temperatures which ranged from 3.9 to 5.0°K and which were increased by annealing the specimens. Parkinson, Simon, and Spedding[6] found by specific heat measurements the transition, not perfectly sharp, at 4.37°K. Earlier work by Allen, McLennan, and Wilhelm[7] on the electrical conductivity indicated no superconducting transition down to 1.5°K. There is no doubt that the transition temperature is affected by many factors and that the explanation of the observed differences is not a simple one.

In the present investigation, the transition temperature, T_s, was taken at the mid-point of then early 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 II. The transition temperatures for both samples are higher than previously reported values, and in only one other case has such a large transition range as that reported here been found.[5] This is perplexing in view of the fact that many of the specimens used by these workers were obtained from this laboratory.

Factors which appear significant as causes for the varied results are the method for detection and the grain size, purity, state of strain, and crystal structure of the samples. The samples described here were as pure as those used by others and in some cases considerably better so this does not seem to resolve the difficulty. 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 II, reannealing the rod after the second run did not change the range.

B. Cerium

A transition in cerium has been observed at approximately liquid nitrogen temperatures by Owen,[8] Trombe,[9] Trombe and Foex,[10,11] Schuch and Sturdivant,[12] and by Parkinson, Simon, and Spedding.[6] It has been shown[13] by the application of pressure that the normal f.c.c. modification of cerium (lattice constant $a=5.140$A) undergoes a transformation to a condensed f.c.c. form

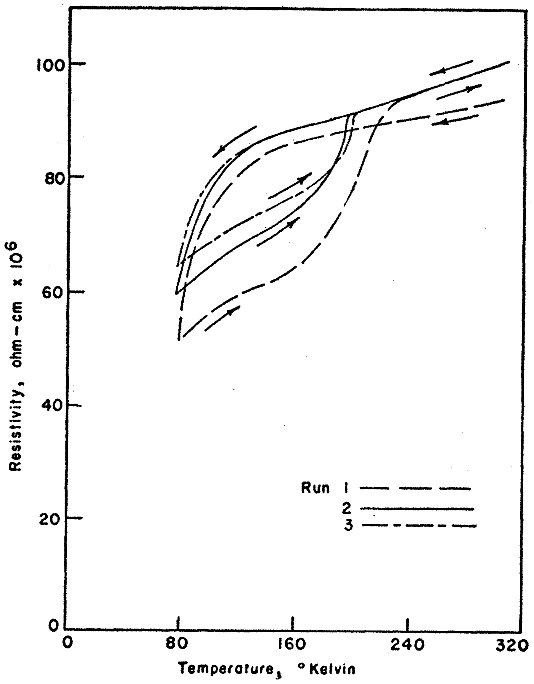

FIG. 4. Resistivity of cerium I as a function of temperature above 78°K.

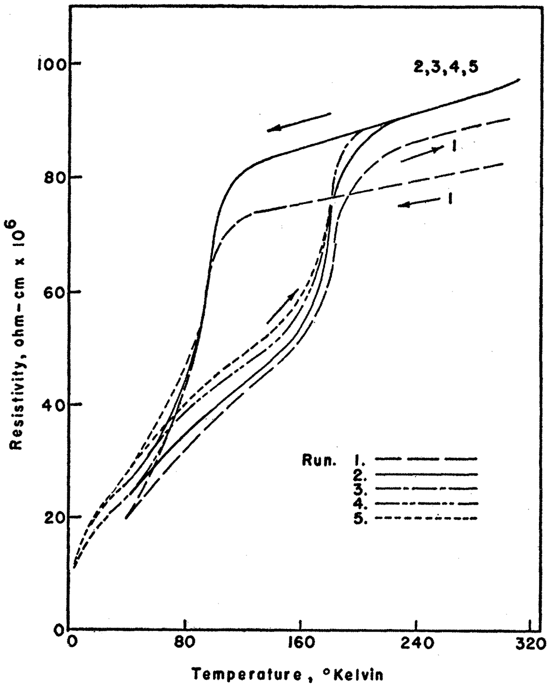

FIG. 5. Resistivity of cerium II as a function of temperature.

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[4] W. T. Ziegler, J. Chem. Phys. **16**, 838 (1948).

[5] Ziegler, Floyd, and Young, O.N.R. Tech. Report No. 2. Georgia Inst. Tech. State Eng. Exp. Station (unpublished) (1950).

[6] Parkinson, Simon, and Spedding, Proc. Roy. Soc. (London) **A207**, 137 (1951).

[7] Allen, McLennan, and Wilhelm, Phil. Mag. **10**, 500 (1930).

[8] M. Owen, Ann. phys. **37**, 657 (1912).

[9] F. Trombe, Compt. rend. **198**, 1591 (1934).

[10] F. Trombe and M. Foex, Compt. rend. **217**, 501 (1943).

[11] F. Trombe and M. Foex, Ann. chim. **19**, 417 (1944).

[12] A. F. Schuch and J. H. Sturdivant, J. Chem. Phys. **18**, 145 (1950).

[13] A. W. Lawson and T. Tang, Phys. Rev. **76**, 301 (1949).

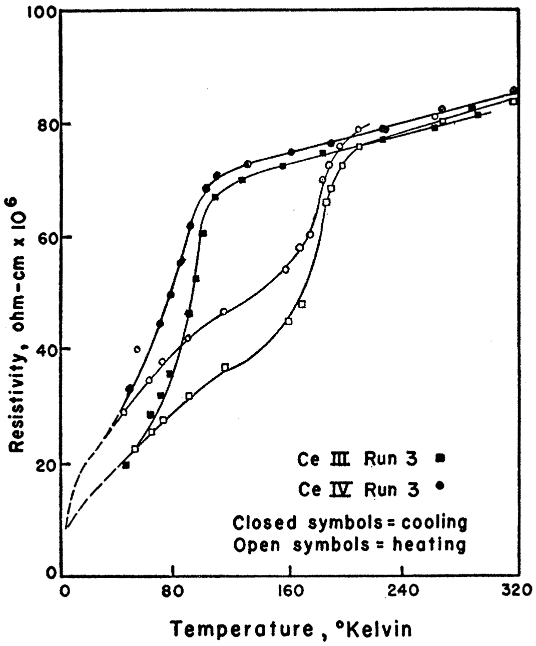

FIG. 6. Resistivity of cerium III and cerium IV as a function of temperature.

(lattice constant $a=4.84\pm0.03$A). The transition was attributed to a shift of a $4f$ electron to a $5d$ orbit. It has also been shown[6,12] that the same transition is temperature induced, and the latter reported smaller proportions of the condensed form appearing on successive coolings.

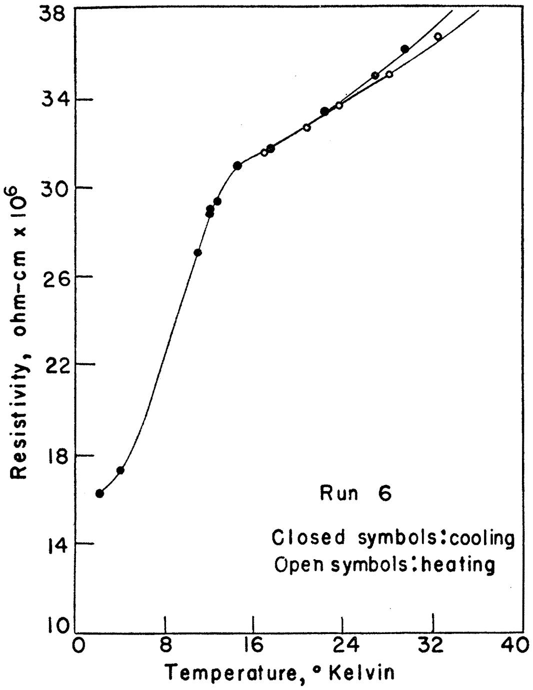

FIG. 7. Resistivity of cerium I as a function of temperature below 40°K.

Cerium has also been found to exhibit anomalous behavior at lower temperatures. Slight hysteresis in the magnetic susceptibility was observed by Starr and Kaufmann[14] at 13.9 and at 20.4°K. A peak in the atomic heat *versus* temperature curve,[6] centered about 11.5°K for one specimen, about 12.5°K for a second specimen, was attributed to a splitting of the lowest energy level of the ion by the field of its neighbors and a consequent redistribution of the electrons among the states.

In the present investigation, all specimens showed on cooling a sudden decrease in resistivity which began at a temperature between 100 and 120°K and which probably corresponded to the transition from the normal f.c.c. structure to the more compact f.c.c. form. The data are shown in Figs. 4, 5, and 6. The corresponding increase in resistivity became apparent, during heating, at approximately 170°K and was complete at approximately 220°K giving the appearance of a hysteresis loop. It should be remarked that this data has not been corrected for changes in density caused by structure changes or by temperature changes.

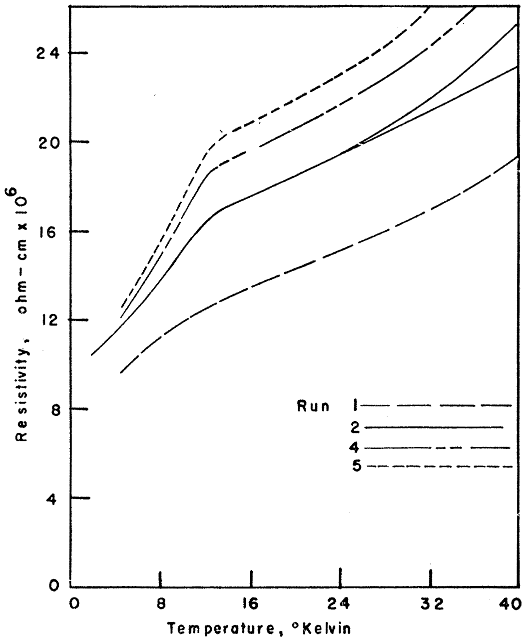

FIG. 8. Resistivity of cerium II as a function of temperature below 40°K.

Ce I, cooled only to liquid nitrogen temperatures during the first three sets of measurements, showed (Fig. 4) a smaller decrease in resistivity each of these times, an effect similar to that observed by Trombe and Foex.[11] 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 f.c.c. form to the h.c.p. An explanation of the smaller

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[14] C. Starr and A. R. Kaufmann, Phys. Rev. **58**, 657 (1940).

decrease in resistivity at liquid nitrogen temperatures with successive thermal cycles is afforded by the slow transition to the h.c.p. structure and the probable inability of that form to undergo a transition to the condensed f.c.c. structure at these temperatures.

At the end of the first set of measurements on each sample, the value of the room-temperature resistivity was higher than it had been at the beginning of the run. With the exception of Ce II (Fig. 5), 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 greater reproducibility of the curves after the first set of measurements may indicate that those microcrystals most easily transformed to the hexagonal form are induced to do so by the first thermal cycle.

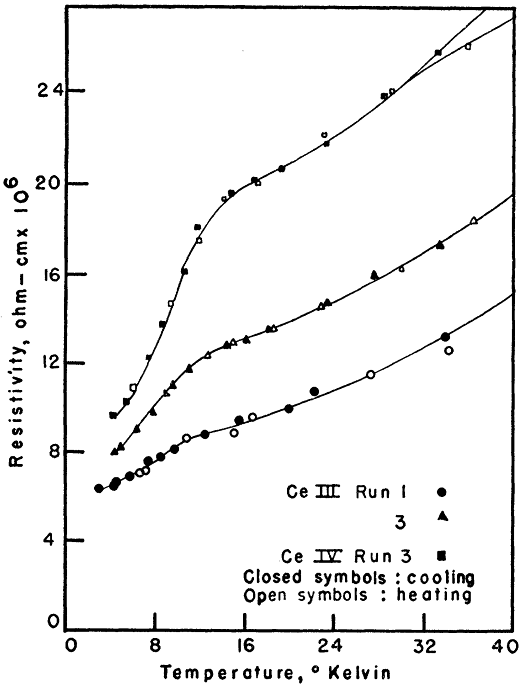

FIG. 9. Resistivity of cerium III and cerium IV as a function of temperature below 40°K.

A second anomalous decrease in resistivity occurred at a temperature between 11 and 14°K. The data for T below 40°K are shown in Figs. 7, 8, and 9. The height of the knees in the curves increased with successive thermal cycles. The cooling rate was approximately the same for each series of measurements. That successive cycles effected more pronounced knees in the curves as well as greater amounts of the hexagonal form suggests the possibility that the h.c.p. crystals transform into the condensed f.c.c. structure (or into a condensed h.c.p. structure) at this lower temperature. The possibility exists that the crystal splitting of the $^2F_{\frac{5}{2}}$ level, which would show a specific heat anomaly near this temperature, may trigger the transition of the $4f$ electron to the $5d$ shell (due to the temperature dependent population distribution of the crystalline electronic structure) and thereby make more probable a crystalline transformation from the room temperature hexagonal

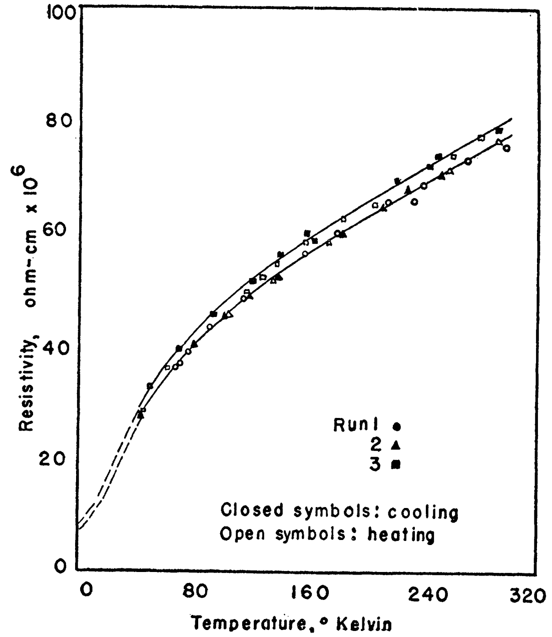

FIG. 10. Resistivity of praseodymium I as a function of temperature.

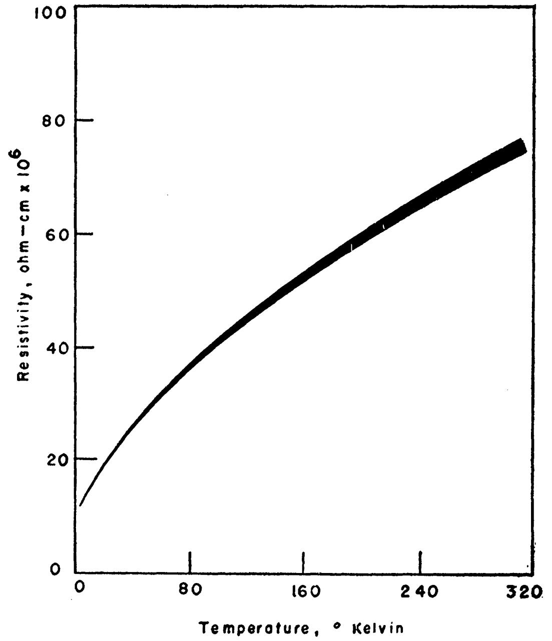

FIG. 11. Resistivity of neodymium I as a function of temperature.

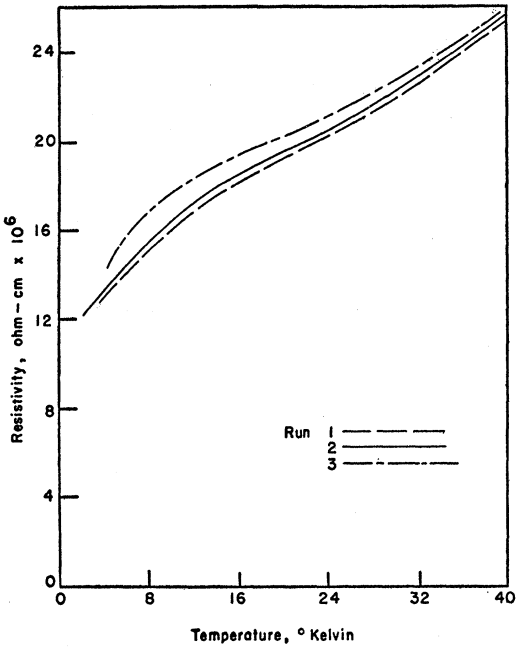

FIG. 12. Resistivity of neodymium I as a function of temperature below 40°K.

form to a condensed cubic or hexagonal form. The onset of ferromagnetism in the hexagonal crystals at this temperature has not been ruled out as an explanation of the anomaly.

The rate of cooling from an annealing temperature to ordinary temperatures has been thought by several investigators[10–12] 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 h.c.p. crystals. Ce IV was cooled in a period of 24 hours and contained a fair amount of the h.c.p. modification. After the third series of measurements the proportion of the h.c.p. form had increased only slightly in Ce III but considerably in Ce IV. A pronounced difference appears in the resistivity curves shown in Figs. 6 and 9. 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 greater knee in the curve appeared at the lower temperature. Again, the curves of Ce III in Fig. 9 show the increase in the low temperature anomaly which accompanies the increase in the amount of the h.c.p. structure. The results here obtained uphold the theory of Trombe and Foex[10,11] that slow cooling after annealing and repeated thermal cycles between room temperature and low temperatures invoke a gradual structural transition. However, in the present investigation, the quenched specimen did not exhibit perfectly reproducible behavior, but transformed also, although at a much slower rate.

C. Praseodymium

The data for praseodymium are shown in Fig. 10. It will be noted that on successive runs an increase in the resistivity occurs which is caused, we believe, by an increase in the amount of the h.c.p. modification. The figure also shows that in the temperature region below 50°K the slope of the curve is considerably greater than that of lanthanum or neodymium. While at present this remains unexplained it suggests the possibility that in this temperature region a gradual transition may be occurring of the cerium type. Investigations on this continue.

D. Neodymium

The behavior of neodymium above 24°K (Fig. 11) was the most reproducible of the rare earths studied. Data for three runs were well within the broad curve shown. Below 24°K an anomaly appeared (Fig. 12) which was centered at approximately 12°K and became more evident with successive thermal cycles. Anomalous peaks in the atomic heat curves appeared at 7 and at 19°K.[6] 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,[6] might well result in a modification of the expected resistivity pattern. Since x-ray analysis showed no f.c.c. crystals present in the sample at room temperature, it is apparent that the low temperature anomaly is not associated with the usual f.c.c. modification.

A comparison of the resistivities of the three h.c.p. (or predominantly h.c.p.) elements (La I, Run 4, Fig. 1; Pr I, Fig. 10; and Nd I, Fig. 11) indicates a decrease in resistivity may occur with an increase in atomic number. 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.

The authors acknowledge their indebtedness to the following members of Dr. Spedding's research group: Mr. J. Powell for the preparation of the pure rare earths; to Mr. J. P. Flynn and Dr. A. H. Daane for the preparation of the rods; to Mr. J. R. Banister and to Dr. V. Fassel's group for the x-ray and spectrographic analyses; and to Mr. R. Anderson and Mr. F. Barson for their assistance in building the apparatus and in taking the data.