FOREWORD

This report was prepared by the Thermal and Solid State Physics Branch, Materials Physics Division of the Air Force Materials Laboratory. The work described was performed by Donald J. Evans under Project 7367, "Research on Characterization and Properties of Materials," Task 736703, "Electronic and Magnetic Properties of Materials."

This report covers work accomplished from 1 May 1962 through 1 May 1964 and was submitted by Mr. Evans in partial fulfillment of requirements for the degree of Master of Science in Physics at Ohio State University.

The author expresses his appreciation to Dr. R. A. Erickson of the Ohio State University for his guidance and counsel during the course of the investigation. Appreciation is also expressed to Westinghouse Electric Corporation for supplying the samples and to members of the Materials Physics Division who participated in many helpful discussions.

ABSTRACT

An apparatus for measuring the electrical resistivity of materials from 4.2°K up to 273.2°K was constructed and used to test niobium zirconium alloys of the following compositions: Nb + 15% Zr, Nb + 25% Zr, Nb + 33% Zr, and Nb + 50% Zr.

It was found that the temperature dependence of the electrical resistivity in these alloys is approximately linear, with Matthiessen's Rule holding for the lower concentrations. The residual electrical resistivity is shown to depend linearly on zirconium concentration.

This technical documentary report has been reviewed and is approved.

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ILLUSTRATIONS

SYMBOLS

ρ	-	electrical resistivity
ρ_o	-	residual electrical resistivity
ρ_T	-	temperature dependent electrical resistivity
ρ_{T_3}	-	electrical resistivity at 273.2°K
T_c	-	critical temperature
PRT	-	platinum resistance thermometer
GRT	-	germanium resistance thermometer
NBS	-	National Bureau of Standards

INTRODUCTION

The objective of this program was to construct an apparatus for measuring the electrical resistivity of materials from 4.2°K up to 273.2°K and to use this apparatus to test several niobium-zirconium alloys which are being used for constructing superconducting solenoids.

The Nb-Zr alloys measured are superconducting and became of interest in 1961 when it was found by Kunzler that they would carry high currents in high magnetic fields (Reference 1). Superconducting Nb-Zr alloys have been found to have useful current densities at fields as high as 80 kilogauss (for example: $J_c > 10{,}000$ amp/cm^2 at 80 kilogauss and 1.5°K (Reference 1).

The critical field of Nb-Zr alloys increases with increasing zirconium concentration, reaches a maximum between 65 and 75 atomic percent zirconium, and then drops quite rapidly. However, the maximum current carrying capacity increases with decreasing zirconium content, reaches a maximum at about 25 percent to 35 percent zirconium, and falls rapidly at lower concentrations (Reference 1). The critical temperature, T_c, increases with increasing zirconium content, reaches a maximum at 20 percent Zr and then slowly decreases (Reference 2).

The phase diagram of Nb-Zr was published in 1955 (Reference 3). Electrical resistivity measurements at 300°K were used as an aid in constructing this diagram and these values are among the few which have been published.

The materials of interest for making solenoids are the Nb + 15% Zr, Nb + 25% Zr, Nb + 33% Zr, and Nb + 50% Zr alloys. Many data have been published concerning these alloys, especially on current carrying capacity as a function of applied magnetic field. The work of Berlincourt, Hake, and Leslie is typical of the studies carried out in this area (References 4 and 5). Work on the microstructure of Nb + 25% Zr alloys has been reported by Walker, Stickler, and Werner (References 5 and 6). Data on the specific heats of transition metal superconductors (Nb + 60% Zr, Nb + 10% Zr, and pure Nb) have been reported by Morin and Maita (Reference 7).

A compilation of the engineering properties of niobium and niobium alloys has been published, but this includes data only on the Nb + 1% Zr and Nb + 5% Zr alloys (Reference 8).

In reviewing the literature, the only electrical resistivity data found were values at 300°K, 273°K, 195°K, 77.3°K, and 1.2°K (References 3, 9, and 10). This report, then, is concerned with measuring the electrical resistivity of Nb-Zr alloys from their transition temperatures up to 273.2°K.

An elementary discussion of the dependence of resistance on temperature will now be given which can be found in Reference 11.

Manuscript released by the author July 1964 for publication as an RTD Technical Documentary Report.

In a perfectly periodic lattice, electrons moving in a given direction will continue to move in that direction indefinitely. A perfect lattice therefore has no resistance. If, however, the crystal lattice is not perfectly periodic, the electrons will be scattered and it is from this scattering that electrical resistivity arises. The departures from periodicity in the crystal which produce electronic scattering and hence electrical resistance may be summarized as follows:

1) The displacement of atoms from their mean equilibrium position in the lattice due to their thermal motion.

2) The presence of foreign atoms in solid solution or of displaced atoms or vacant lattice sites.

3) The breakdown of the solid in going to liquid or amorphous states.

The classical free electron model of metals yields an expression for the electrical conductivity, σ, of the following form:

$$\sigma = \frac{F}{i} = \frac{Ne^2\tau}{m} \qquad (1)$$

where

F = electric field in the metal

i = resultant electric current density in the metal

N = number of free electrons per unit volume

e = electronic charge

τ = mean scattering time

m = electron mass

For normal metals and alloys the bulk resistivity can be generally represented according to Matthiessen's Rule as the sum of two parts:

$$\rho = \rho_0 + \rho_T \qquad (2)$$

where ρ_0 is the "residual resistance" arising from the scattering of conduction electrons by lattice imperfections such as foreign atoms, grain boundaries, dislocations, strains, and so forth, and ρ_T is the temperature dependent resistance arising from the interaction of conduction electrons with the thermal vibrations of the metallic ions.

Considerable work has been done on the theory of electrical conductivity in dilute alloys by Norbury (Reference 12), Linde (Reference 13), Meissner and Voigt (Reference 14), DeHass and van den Berg (Reference 15), and MacDonald and Pearson (Reference 15) to mention a few.

The Nb-Zr alloys which were measured in this investigation were not dilute but would fall into the category of comparable concentration of both components. This situation is briefly discussed in Reference 11. The authors there assumed that the alloy under consideration consists of a single phase. As explained previously the resistance of the alloy can be divided into two parts ρ_0 and ρ_T. For these alloys the term ρ_T is, in general, linear in T, and assuming that no superlattice is in process of formation, one may write:

$$\rho_T = T \frac{d\rho}{dT} \qquad (3)$$

Generally speaking, Matthiessen's Rule holds as long as the temperature independent part of the resistance is small compared to the temperature dependent part, and as long as the introduction of none of the components affects considerably the lattice of the solvent metal (Reference 17). For concentrations of solute metals exceeding, for instance, 5 percent in some cases, and for higher concentrations in all cases, the deviation from the assumed normal additivity of the impurity resistance becomes so large that the applicability of Matthiessen's Rule is doubtful.

For Nb-Zr alloys, one of the following rules of LeChatelier and Guertler (Reference 17) should apply depending on whether the alloys are single phase or a mixture of phases:

1) The electrical conductivity and its temperature coefficient of heterogeneous mixtures of two phases vary linearly with the composition, measured in volume percent.

2) The electrical conductivity and its temperature coefficient for solid solutions are always below those of the solvent metal and for continuous solid solutions the conductivity is a U-shaped curve in the conductivity-composition diagram.

APPARATUS

GENERAL DESIGN

The apparatus had to be suitable for measuring the electrical resistance of wire samples from 4.2°K up to 273.2°K. Thus a system had to be designed which could be cooled to liquid helium temperature and which would then rise continuously up to room temperature. No provision was made for holding a certain temperature for a prolonged period since the apparatus was made to record continuously all the variables of interest.

The Dewar used is made of glass, is silvered except for one strip, and has a capacity of about 5 liters. A 5 mV full scale, 12 point Brown recorder was chosen for recording all parameters except the voltage drop across the sample and for this a 100 μV full scale Brown recorder is used. In the temperature range 4.2°K to 100°K a germanium resistance thermometer is used as the temperature sensing element. In the range 77°K to 273.2°K a copper-constantan thermocouple is used. A calibration of the apparatus was made by measuring the resistance of a platinum sample as a function of temperature.

A photograph of the apparatus is shown in Figure 1.

The sample holder is made of fiber board and is shown in Figure 2. Current is supplied through brass spring contacts. The voltage drop is obtained through razor blade contacts which were made by soldering pieces of a razor blade into the slot in a round headed screw. These contacts are held in place by six small springs. A hole in the fiber board under the sample allows one to place the thermocouple in contact with the sample. A solid copper cylinder of about 250 grams is attached to the upper end of the sample holder. The purpose of the copper block is to thermally anchor all the leads coming from the sample and to absorb the heat being conducted into the system in order to slow the temperature rise of the sample. The copper block was threaded on the outside and all leads (.005 inch copper

Figure 1. Low Temperature Electrical Resistivity Apparatus

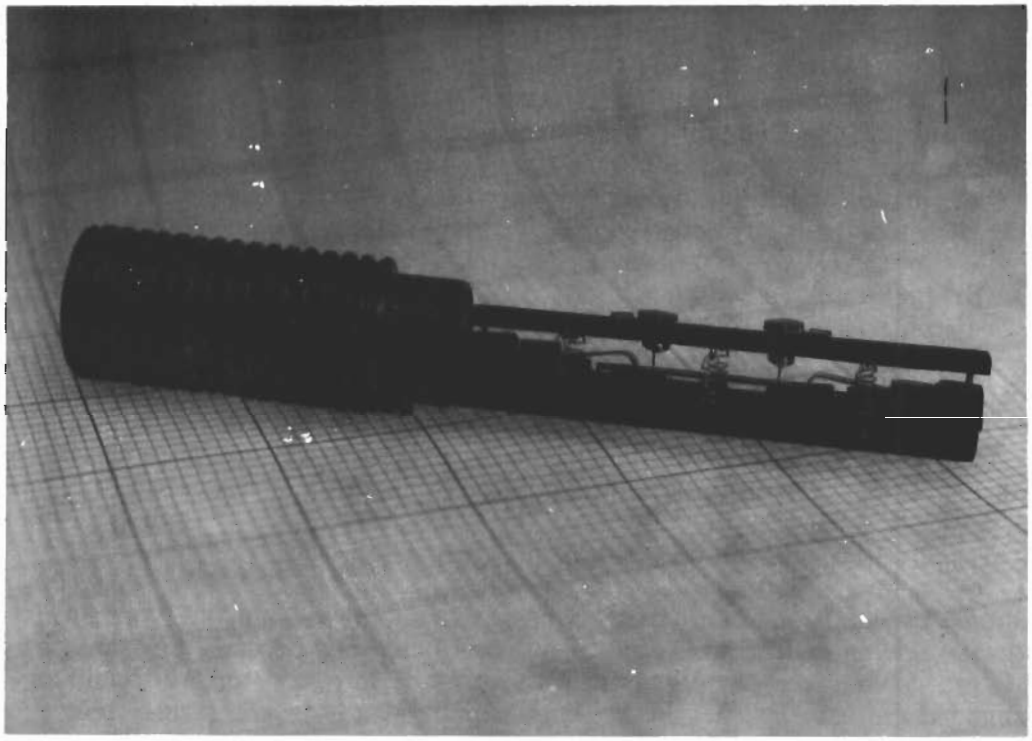


Figure 2. Sample Holder

wire) were glued into the thread grooves using Duco cement. White tape was then used to wrap the block. Surrounding the sample holder and attached to the copper block is a copper cylinder of 7/8 inch I.D. which is used to maintain all parts of the sample holder at equilibrium temperature.

To contain the sample holder, the stainless steel tube, 24 inches long, shown in Figure 3 is used; it is 1 1/4 inches O.D., has a wall thickness of 1/32 inch. An inlet in the side of this tube serves as a connection to the helium gas line or the vacuum line. The tube is sealed at the top by use of a rubber "O" ring. Soldered into the center of the top disk is a Stupakoff seal which serves to admit the necessary wire leads to the sample. The wires are sealed in by using black wax. The sample holder is suspended from the top by a 17-inch length of phenolic tubing.

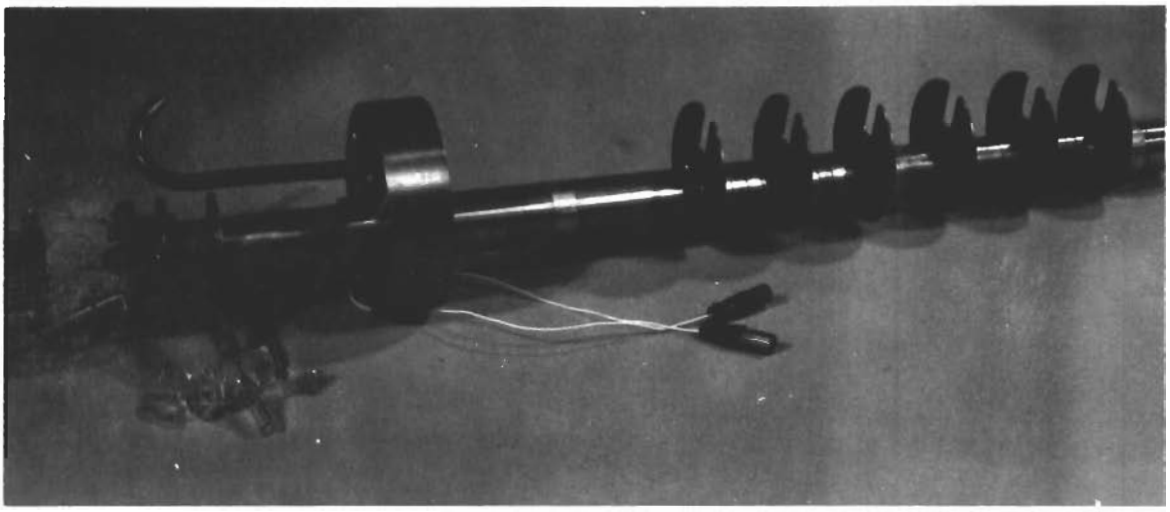


Figure 3. Sample Container

A gold plated connector is located on top of the stainless steel tube and all wires coming from the sample holder are attached to it. This enables one to quickly disconnect all leads from the sample container. All other connections were made with the use of low thermal emf solder.

Copper disks were placed on the stainless steel tube so that it could be more efficiently cooled. The slots were cut in these disks to accommodate the helium transfer tube.

A heater was wound around the outside of the sample container to heat the sample after it was cooled to 4.2°K. The heater consisted of 10 feet of .005 inch Manganin wire whose resistance is 11.7 ohms per foot.

RESISTIVITY MEASURING CIRCUIT

The circuit for measuring electrical resistivity is shown in Figure 4. The circuit consists of a 1.5 V dry cell, a 3000 ohm variable resistor to control the current, a 0.5 ohm standard resistor, and an ammeter to give a visual indication of a complete circuit and also serve as a rough estimate of current magnitude. The voltage drop across the standard resistor is measured with a 5 mV full scale multi-point recorder. To record the voltage drop across the sample, a 100 μV full scale Brown recorder is used. Both recorders have a chart speed of 8 inches per hour. Previously an attempt was made to use one of

the inputs to the multi-point recorder in conjunction with an amplifier for recording the voltage drop across the sample. However, no amplifier with low enough noise level was available.

Ohm's Law is used to compute the resistance of the samples.

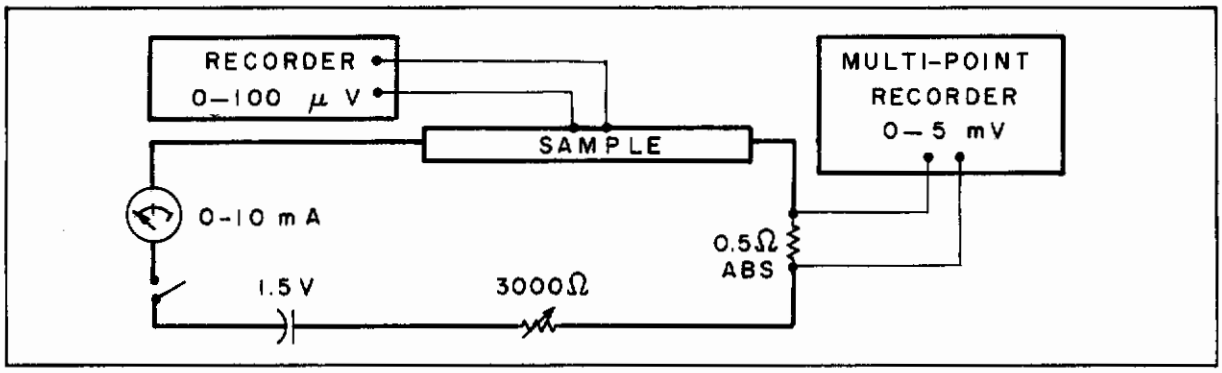
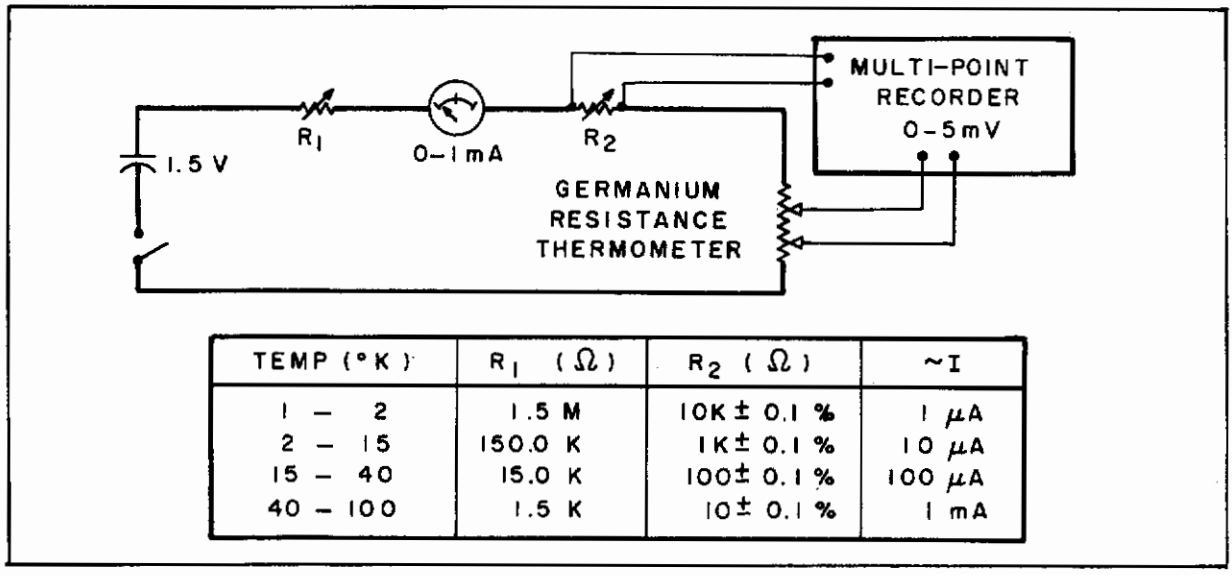


Figure 4. Electrical Resistivity Measuring Circuit

TEMPERATURE MEASURING CIRCUIT

The circuit for measuring temperature using the germanium resistance thermometer is shown in Figure 5. This circuit consists of a 1.5 V dry cell, a variable resistor to adjust the current and a decade resistor to measure the current. Figure 5 also indicates the approximate values of the resistances for various temperature ranges. The voltage drops across both the Ge element and the standard resistor are recorded on the 5 mV multi-point recorder.

The thermocouple was made from 36-gauge copper and constantan wires. The reference junction is in a slush bath of ice and water. An L & N type K-2 potentiometer is used to supply the bias voltage when the thermocouple output exceeds 5 mV.



TEMP (°K)	R_1 (Ω)	R_2 (Ω)	~I
1 – 2	1.5 M	10K ± 0.1 %	1 μA
2 – 15	150.0 K	1K ± 0.1 %	10 μA
15 – 40	15.0 K	100 ± 0.1 %	100 μA
40 – 100	1.5 K	10 ± 0.1 %	1 mA

Figure 5. Measuring Circuit for Germanium Resistance Thermometer

SAMPLE DESCRIPTION

The Nb-Zr samples tested in this investigation were supplied by Westinghouse and were of the following compositions: Nb + 15 weight percent Zr, Nb + 25% Zr, Nb + 33% Zr, and Nb + 50% Zr. These compositions vary by ±1% Zr along the length and/or along a radius of the wire. The samples were in bare wire form of the following sizes: 15 mil for the 15% Zr and 25% Zr, 7.5 mil for the 33% Zr, and 9.8 mil for the 50% Zr. The samples were 1 1/2 inches long.

The NbZr alloys were prepared from electron beam grade Nb and iodide crystal bar Zr and in general were fabricated using the following technique. Samples were hot extruded, then cleaned and cold worked by swaging. They were subsequently recrystallized and again cold swaged to final wire size. Reduction by cold working was 99.96 percent.

These alloys were analyzed using X-ray diffraction to determine the lattice constants. The results are shown in Figure 6. Values of the lattice constant obtained were 3.345 Å, 3.368 Å, 3.385 Å, and 3.435 Å for the 15% Zr, 25% Zr, 33% Zr, and 50% Zr samples, respectively. Figure 7 shows that the lattice parameter varies linearly with composition in agreement with Vegard's Law. Although none of the data obtained indicate the presence of a second phase, Westinghouse is of the opinion that there is usually a small amount (< 4%) of a second phase present.

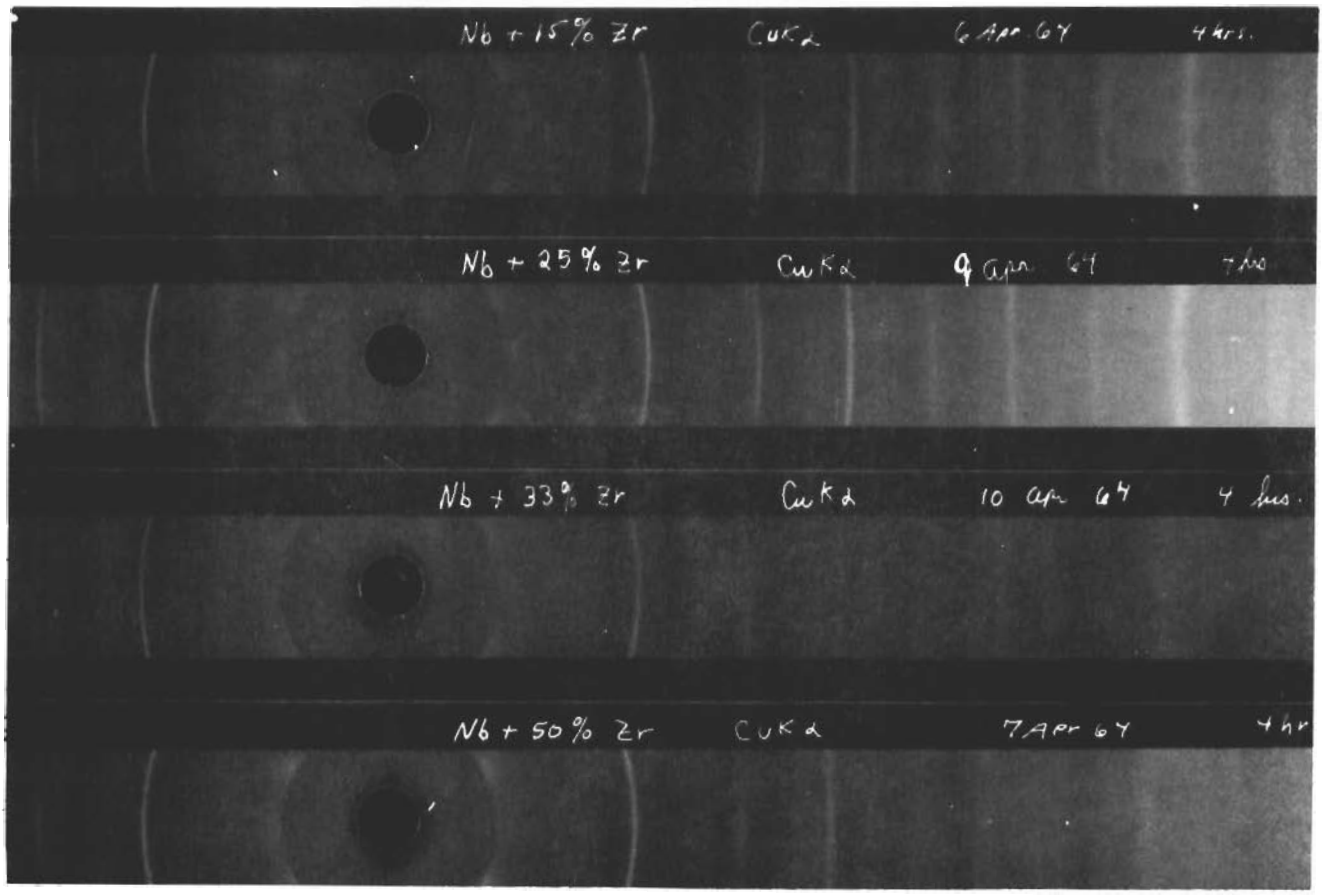


Figure 6. X-Ray Diffraction Patterns for Nb-Zr Alloys

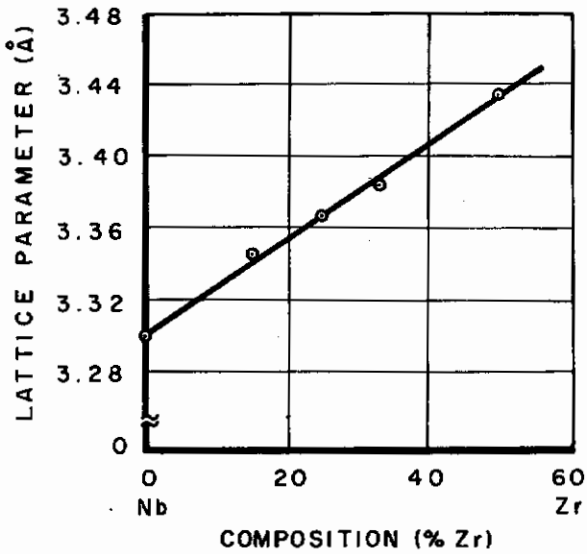


Figure 7. Lattice Parameter vs. Atomic Percent Zr for Nb-Zr Alloys

Spectrographic analysis of the Nb-Zr samples revealed the metallic impurities listed in Table 1. Analysis for interstitial impurities in the alloys was done by Westinghouse on the ingots and these impurities are also listed in Table 1.

TABLE I
IMPURITY ANALYSIS OF Nb – Zr SAMPLES

SAMPLE	ELEMENTS DETECTED (ppm)									
	Al	Fe	Mg	Mo	Ni	Si	O	N	H	C
Nb + 15 % Zr	50	50	100	200	10	60	70-150	15-40	< 5	< 60
Nb + 25 % Zr	50	100	50	60	10	60	70-150	15-40	< 5	< 60
Nb + 33 % Zr	150	150	35		15	110	70-150	15-40	< 5	< 60
Nb + 50 % Zr	150	120	15		15	75	70-150	15-40	< 5	< 60

The Nb sample was obtained from a roll of 24.9 mil wire available in the laboratory. Its source is not known. Spectrographic analysis of the Nb sample revealed 10 ppm each of Mg, Mo, Ni, and Ti, 20 ppm Fe, 30 ppm Si, and 5 ppm Zr. The Pt sample was a piece of 16 mil thermocouple wire from Baker Platinum Division of Engelhard. Spectrographic analysis of the Pt sample revealed 10 ppm each of Ag, Fe, Mo, and Pd. The Nb and Pt samples were not analyzed for gaseous impurities.

EXPERIMENTAL PROCEDURE

GENERAL DISCUSSION

First, the sample was placed in the holder and the voltage drop was checked to see that the probes were in good contact. The sample container was then evacuated using only a forepump. After evacuation, the sample container was filled with helium to an overpressure of approximately 2 psi. The sample holder was then placed in a Dewar of liquid nitrogen for pre-cooling prior to transfer to the helium Dewar.

The inner (helium) Dewar was evacuated using only a forepump. The sample container was placed in the inner Dewar and the outer Dewar was filled with liquid nitrogen. After waiting about two hours, the liquid nitrogen was replenished, the transfer tube evacuated, and the liquid helium transferred into the inner Dewar. A pressure of 2 psi of gaseous helium was used to effect the transfer. Between 2 1/2 and 3 liters of helium were required to cool the sample container to 4.2K. The transfer usually took about 3 minutes.

The recording system was connected and the run started.

While the Dewars were cooling, an ice junction was made for the thermocouple reference. A potentiometer provided the bias voltage when the thermocouple emf exceeded 5 mV. At less than 5 mV the potentiometer was not used. The potentiometer was usually calibrated four times but was found to vary only slightly. During the run the current in the resistance thermometer had to be changed three times, because of the large resistance change with temperature.

Originally the system warmed up too slowly; therefore a resistance heater was used. The heater was powered by an auto-transformer, which was usually increased in increments of 10 volts. The maximum voltage used was 60 at which time about 0.5 amp was flowing in the heater circuit.

A run required from three to four hours to complete.

ERROR ANALYSIS AND CALIBRATION

Electrical resistivities in ohm-cm were calculated using the relation:

$$\rho = R \frac{A}{L} \tag{4}$$

where A = the cross-sectional area in cm^2 of the sample, L = the distance in cm between voltage drop probes, and R = the resistance in ohms of the sample calculated from Ohm's Law:

$$R = \frac{E}{I} \tag{5}$$

where E= the voltage drop in volts across the sample and I = the current in amperes through the sample.

Probable errors in the measurement of the above quantities will now be discussed. The separation of potential contacts was measured to the nearest .002 in. which would introduce an error of about 0.2 percent. The diameter of the samples was measured to the

nearest .0001 in. which would account for an error of around 0.2 percent. The current was measured with a 5 mV recorder which could be read to the nearest 0.02 mV or an accuracy of 0.4 percent at 5 mV and 2 percent at 1 mV. The standard resistor used in this measurement was accurate to 0.01 percent which is a negligible error. The potential drop was measured with a 100 μV recorder which could be read to the nearest 0.25 μV or an accuracy of 0.25 percent at 100 μV and 2.5 percent at 10 μV.

In calculating the resistance of the germanium thermometer, Ohm's Law was again used. The current and potential drop were measured with the 5 mV recorder and were read to an accuracy of between 0.4 percent and 2 percent. The temperature variation at 10°K assuming an error of 2 percent in the resistance would be less than 0.1°K. At 100°K the error would amount to about 1°K. An error of 0.1 mV in reading the thermocouple output would amount to an error of 0.5°K at 100°K and about 0.25°K at 273.2°K.

Other errors could have been introduced by the connector at the top of the sample container, by thermal emf's in the system, and in a variation in the temperature of the ice bath. Since it would be difficult to attach values to the error introduced by these sources, it was felt that an estimate of the accuracy of the measurement could best be obtained by measuring a well characterized material such as platinum.

In order to calibrate the apparatus, the dependence of resistance on temperature was determined for a platinum sample as shown in Figure 8. The absolute value of resistivity falls within the range of room temperature values given in Reference 18. Values of ρ_T/ρ_{T_3} were determined from the resistance measurements. Values of R_T/R_{T_3} were also computed for a platinum resistance thermometer (PRT) which was calibrated by the National Bureau of Standards (NBS). The two sets of values were plotted as a function of temperature from 80°K to 300°K and are shown in Figure 9.

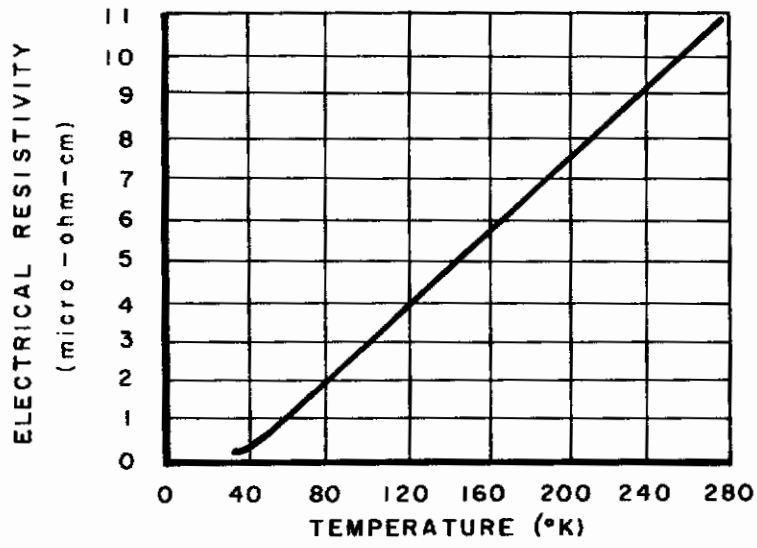


Figure 8. Electrical Resistivity vs. Temperature for Pt Sample

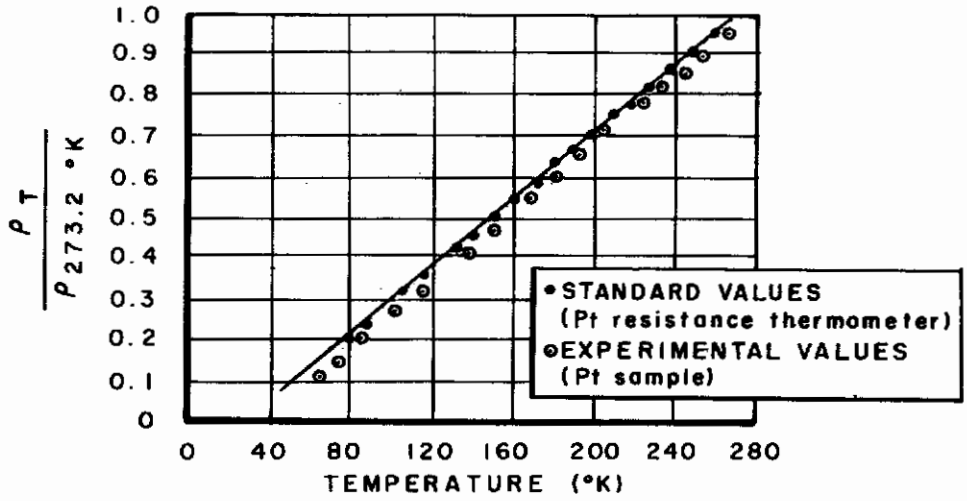


Figure 9. Resistivity Ratio vs. Temperature for Pt Sample

Assuming the temperature measurement to be correct (the justification for this assumption follows) one can determine the accuracy of the resistivity measurement. At 150°K the deviation from the NBS data is about 4 percent. As discussed later in the section on experimental results, the deviation of values of resistivity for Nb + 25% Zr from the values reported by Westinghouse (Reference 9) was within this 4 percent range.

The temperature was checked in several ways. In the first place, the germanium resistance thermometer (GRT) was calibrated from 1.5°K to 100°K by the manufacturer and it is very sensitive especially at the lower temperatures. Although the GRT was not actually in contact with the thermocouple or sample, it is felt that this was not a significant source of error because of the gaseous helium in the sample container in addition to the copper surrounding the sample holder. This matter is discussed in the section on experimental results where the response times of the temperature sensors are shown to be the same.

The copper-constantan thermocouple output was converted to temperature using the data compiled from "Low Temperature Thermocouples", by R. L. Powell, National Bureau of Standards, and it agreed with the GRT within 1°K from about 35°K on up to 100°K.

For one check on the thermocouple, the GRT, the PRT, and the thermocouple were all placed in a Dewar of liquid nitrogen. Values of temperature obtained were 77.3°K, 77.4°K, and 77.7°K respectively.

To check the calibration of the thermocouple at higher temperatures, the PRT and the thermocouple were immersed in a slush bath of ethyl bromide (C_2H_5Br) in liquid nitrogen. Ethyl bromide freezes at approximately 153°K, so the thermocouple was calibrated from 153°K to 246°K using this technique. The resistance of the PRT was measured using a Mueller bridge. The thermocouple output was recorded on the 5 mV Brown recorder in the same manner in which it was done during actual experiments. The results are shown in Table 2, where T_1 is the thermocouple temperature, T_2 is the PRT temperature, and $\Delta T = T_1 - T_2$.

TABLE 2
THERMOCOUPLE CALIBRATION

T_1 (°K)	T_2 (°K)	ΔT (°K)	T_1 (°K)	T_2 (°K)	ΔT (°K)
153.8	153.6	0.2	193.06	192.8	0.26
154.2	153.8	0.4	208.5	208.3	0.2
154.2	153.6	0.6	209.4	209.2	0.2
154.4	153.7	0.7	225.8	225.7	0.1
154.4	153.8	0.6	226.56	226.7	-0.14
159.86	159.6	0.26	239.76	240.0	-0.24
161.7	161.6	0.1	240.6	240.8	-0.2
164.3	164.0	0.3	244.4	244.5	-0.1
169.36	169.0	0.36	244.5	244.5	0.0
178.8	178.4	0.4	245.5	245.6	-0.1
179.7	179.4	0.3	245.9	246.0	-0.1

Considering (1) the values of resistivity at 273.2°K for Pt and Nb, (2) the values of room temperature resistivity for Nb-Zr alloys as reported by Rogers and Atkins (Reference 3), (3) the values of resistivity for Nb + 25% Zr alloys given by Westinghouse for these different temperatures, and (4) the values of resistivity ratios for Pt, the estimated accuracy of the resistivity measurement is 4 percent.

From comparison with calibrated platinum and germanium resistance thermometers and from measurements of the critical temperatures of the superconducting alloys, the error in the temperature measurement is considered to be less than 1°K.

EXPERIMENTAL RESULTS

Before discussing the data obtained on the Nb-Zr alloys, the results of the technique outlined previously will be shown by discussing parts of three experimental runs.

Figure 10 shows the voltage drop measurement for a Nb + 15% Zr sample between 4.25°K and 140°K, and Figure 11 shows the chart on which the associated data are printed. Figure 10 shows that the normal-superconducting transition was passed through three times. The three values of T_c measured were 10.3°K, 10.9°K, and 9.85°K. Figure 11 has all the data labeled but a few comments will be made for clarity. The GRT voltage drop was changing very rapidly in the 4.25°K to 10°K range because of the large change in resistance from 1078 ohms to 182.5 ohms. The values for R_1 and R_2 on the right side of the chart correspond to values of the resistances in the GRT circuit (see Figure 5). The GRT current can be seen to be fairly constant over any one temperature range. Figure 11 also shows that the sample current is constant. About two thirds of the way from the bottom of the chart (at a temperature of about 75°K) one can see where the sensitivity of the GRT decreases and that of the thermocouple increases to the point where it is the more sensitive temperature detector.

Figures 12 and 13 show results of the first successful experiment on Pt. This experiment was performed before the Manganin heater was wound around the sample container. In this case the temperature was increased by directing heated air into the Dewar. This accounts for the irregular temperature rise. These figures were included to demonstrate the response time of the temperature sensors. It is felt that the decrease in resistance shown in Figure 12 and confirmed by the temperature decrease shown in Figure 13 was caused by a sudden evaporation of liquid gases in the tip of the Dewar. This sudden evaporation could have been caused by water falling into the liquid gases; the water having accumulated from the hot air forced into the Dewar. As can be seen from Figure 13, the GRT and the thermocouple both responded at very close to the same time and were of about the same sensitivity at this temperature (~66°K). By comparing the charts in Figures 12 and 13 it can be seen also that the decrease in resistance began at the same time as the temperature sensors showed a change. This indicates that if there was a temperature lag between the sample and the sensors, it was not detectable using this apparatus.

Figures 14 and 15 show an example of the results at the upper end of the temperature range. These figures include data from 53°K to 273°K. Figure 15 shows the nearly linear temperature rise which can be obtained with the apparatus. The resistance minimum of the GRT can be seen at about 190°K.

The results of the measurements made on the Nb and the Nb-Zr samples will now be discussed. These results are shown graphically in Figures 16 through 24. The curve drawn on all the resistivity vs. temperature graphs is a straight line except for the leveling out at the low temperature end. A smooth curve could have been drawn through the data points which would be slightly concave downward. This variation has not been resolved and may indeed be the actual case.

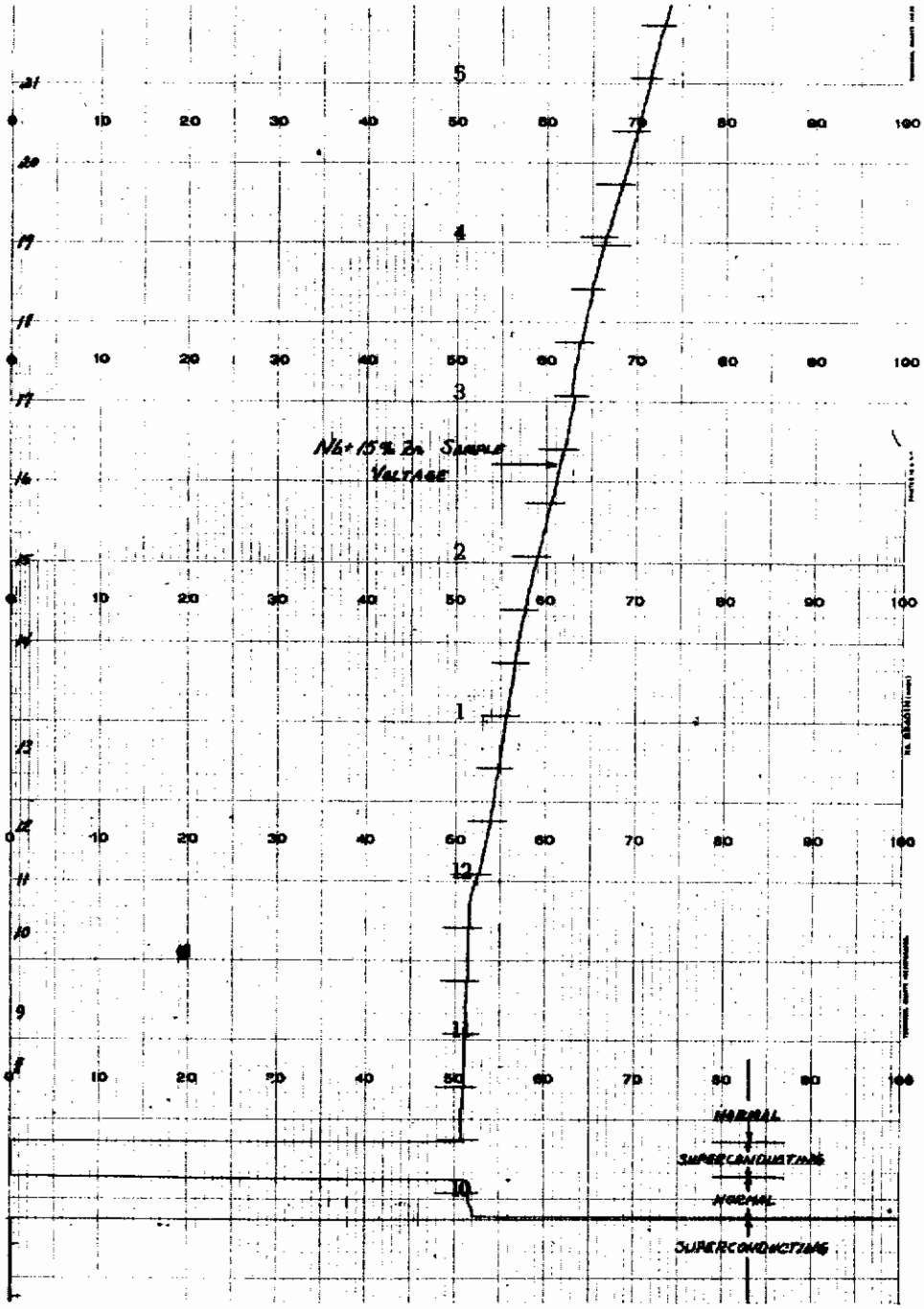


Figure 10. Recorder Chart of Nb + 15% Zr Sample Voltage

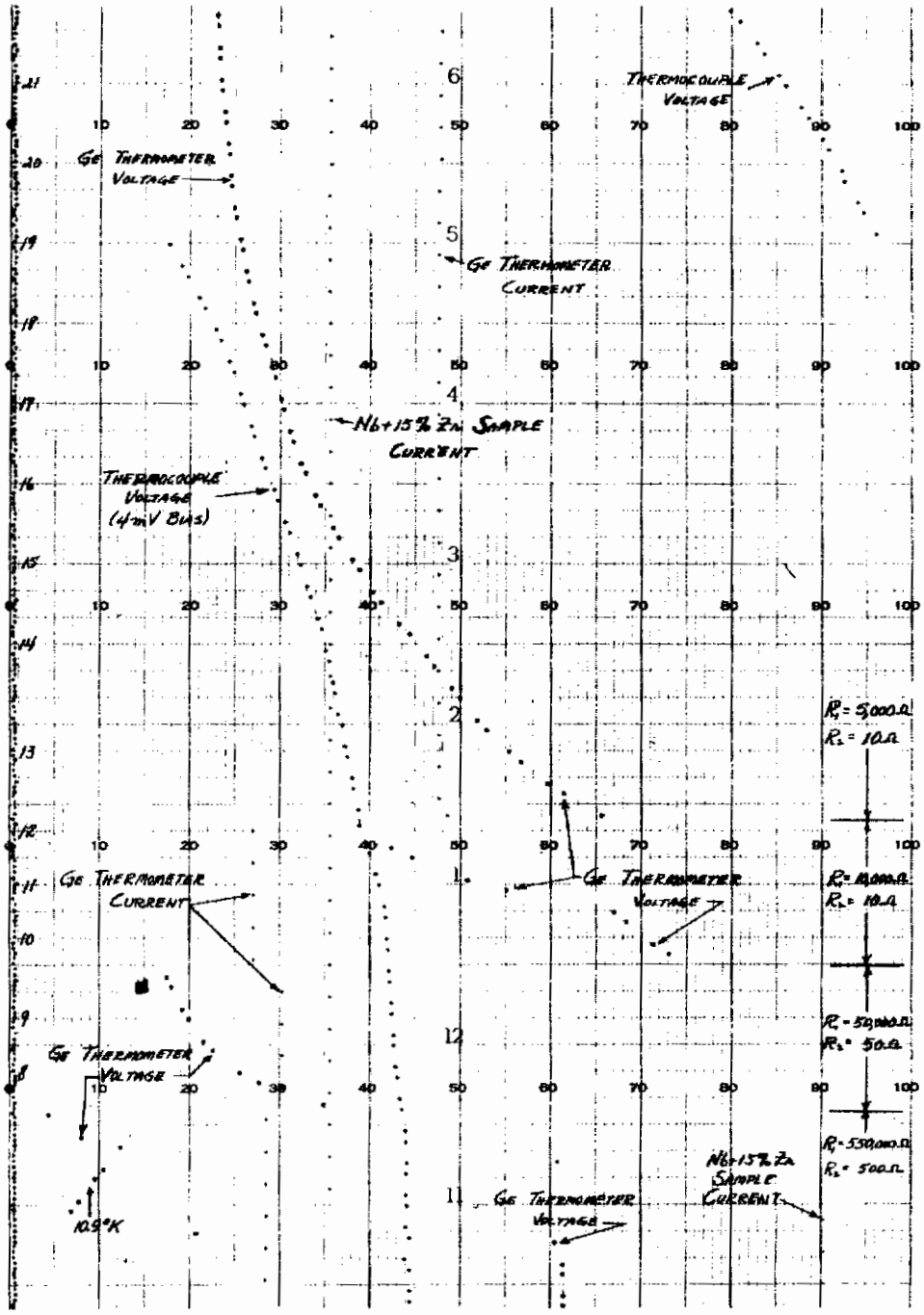


Figure 11. Chart of Recorded Data for Nb + 15% Zr Sample

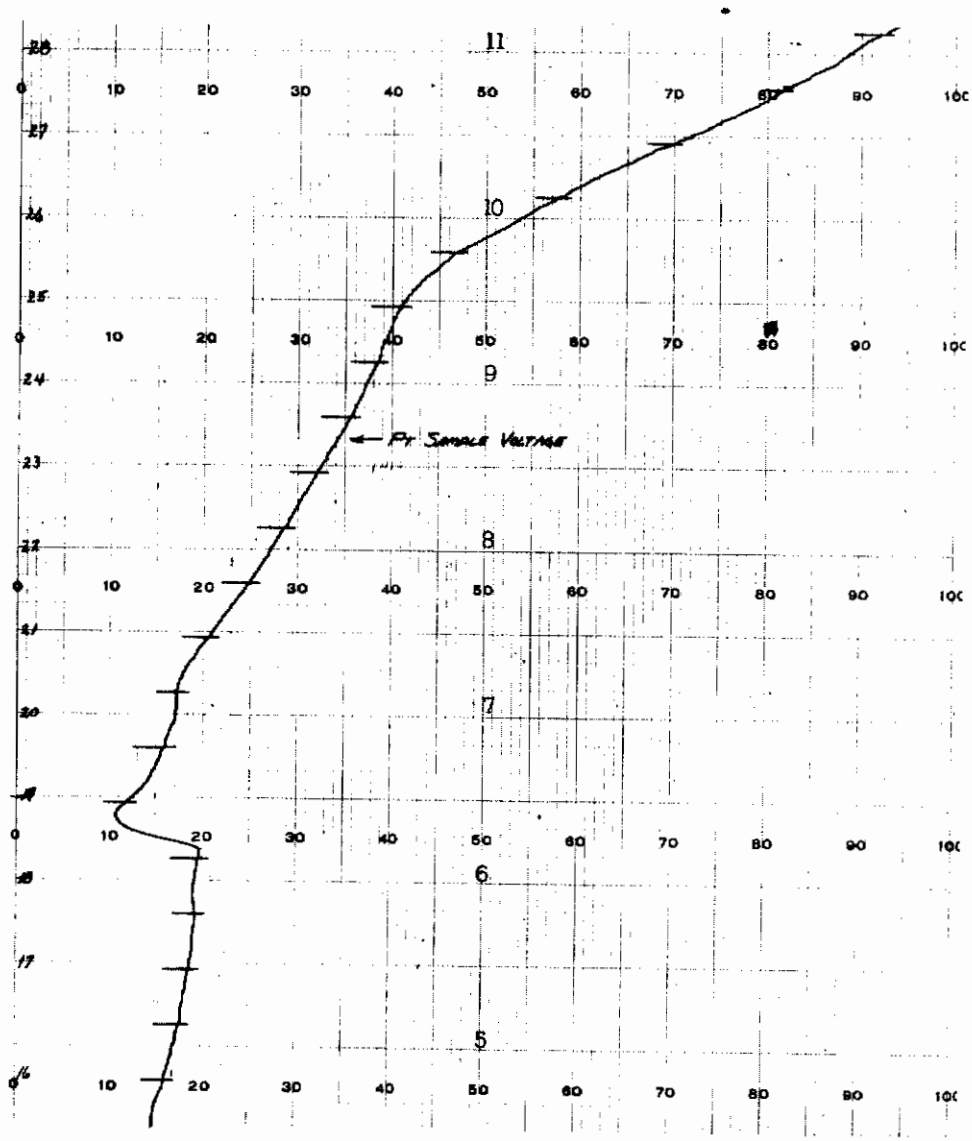


Figure 12. Recorder Chart of Pt Sample Voltage

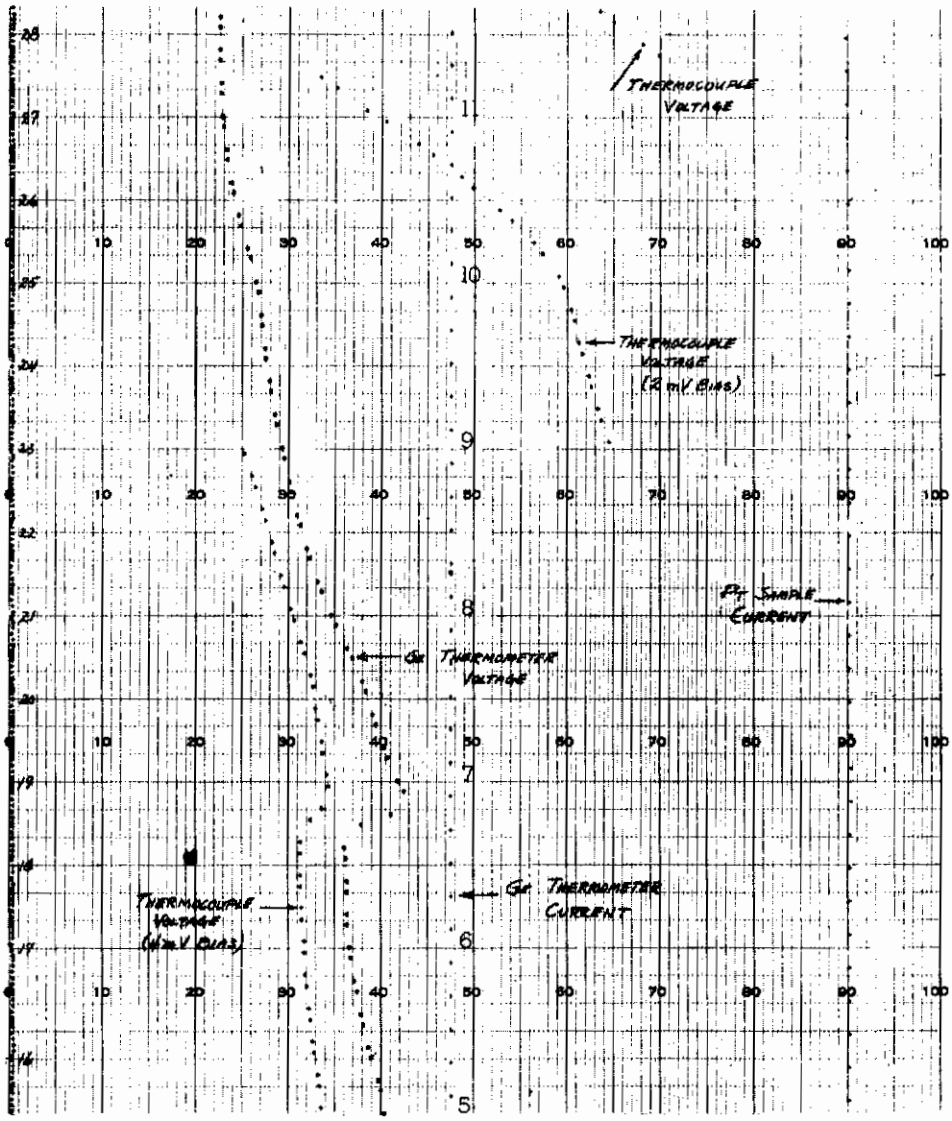


Figure 13. Chart of Recorded Data for Pt Sample

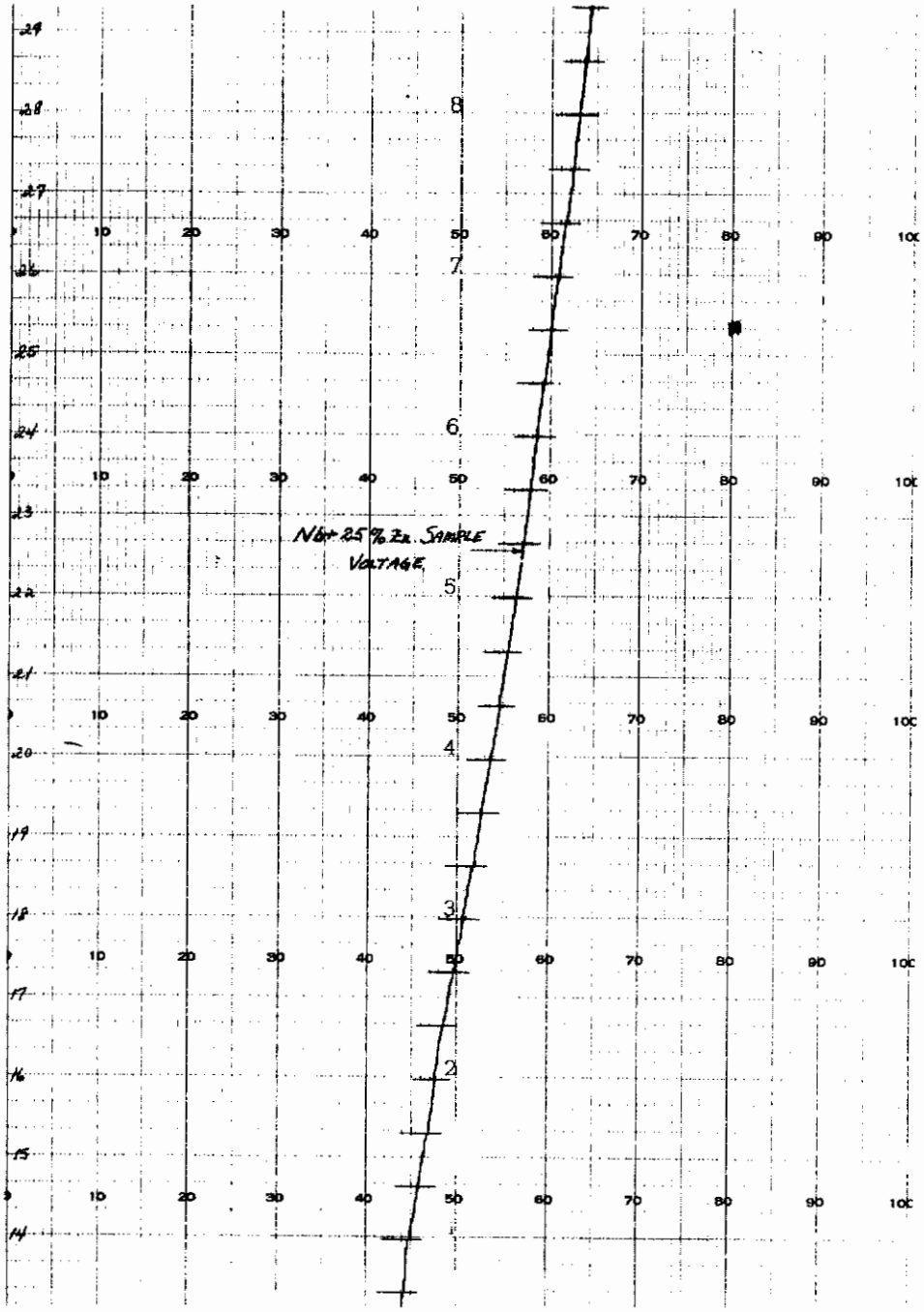


Figure 14. Recorder Chart of Nb + 25% Zr Sample Voltage

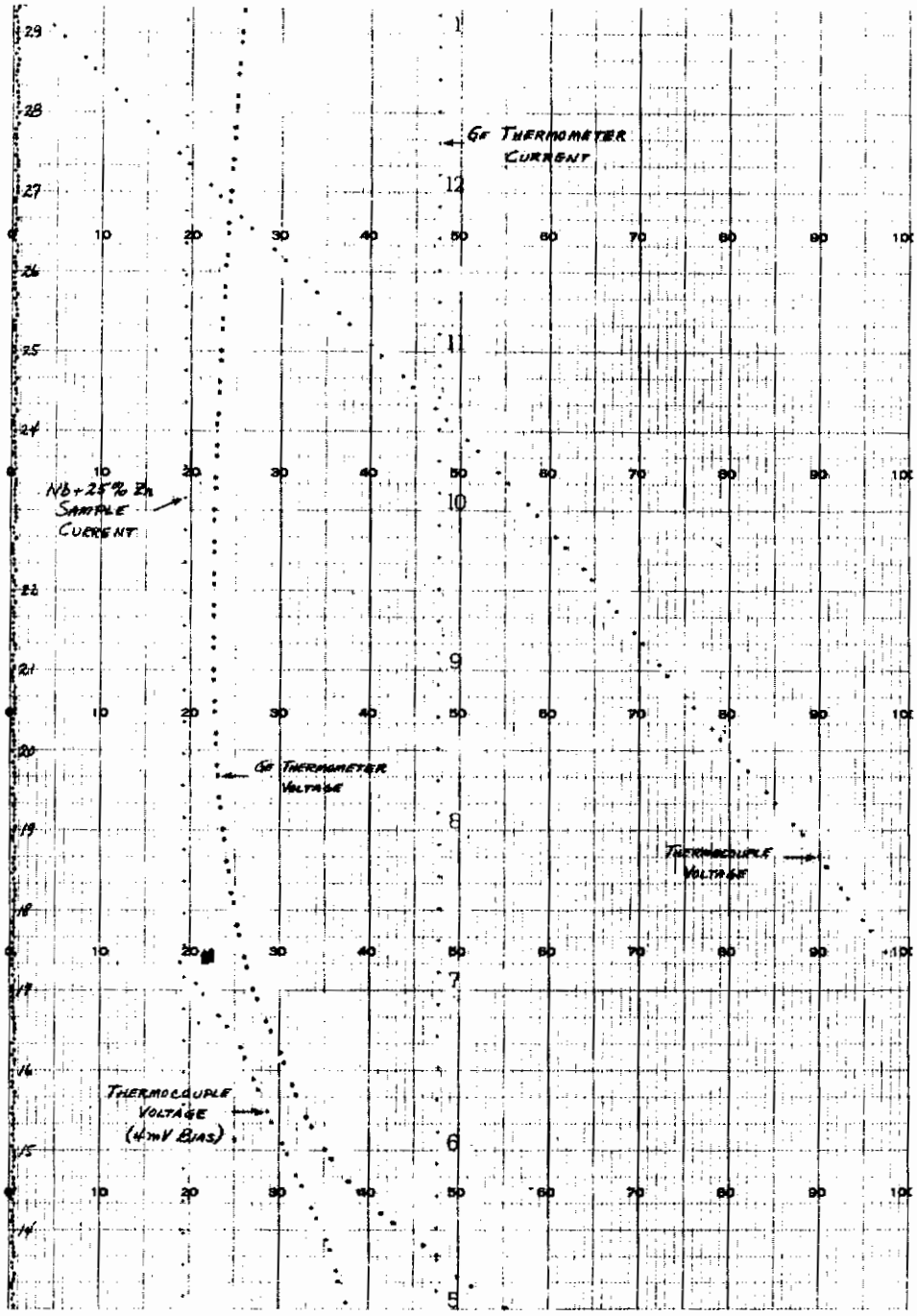


Figure 15. Chart of Recorded Data for Nb + 25% Zr Sample

Figure 16 shows a plot of electrical resistivity versus temperature for Nb. For this sample the T_c measured was 8.35°K, ρ_o was about 2.2 μ-ohm-cm, and ρ_{T_3} was 16 μ-ohm-cm.

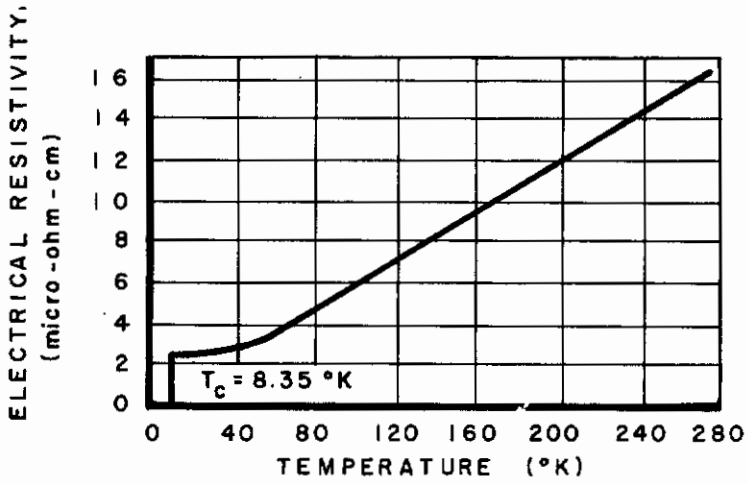


Figure 16. Electrical Resistivity vs. Temperature for Nb Sample

Figure 17 gives the data obtained on the Nb + 15% Zr sample. T_c was measured three times for this sample with values of 10.3°K, 10.9°K, and 9.85°K. The 10.9°K value was the same as the value reported in the literature and was printed on the graph for this reason (Reference 2). For this sample ρ_o = 16 μ-ohm-cm and ρ_{T_3} = 30.3 μ-ohm-cm.

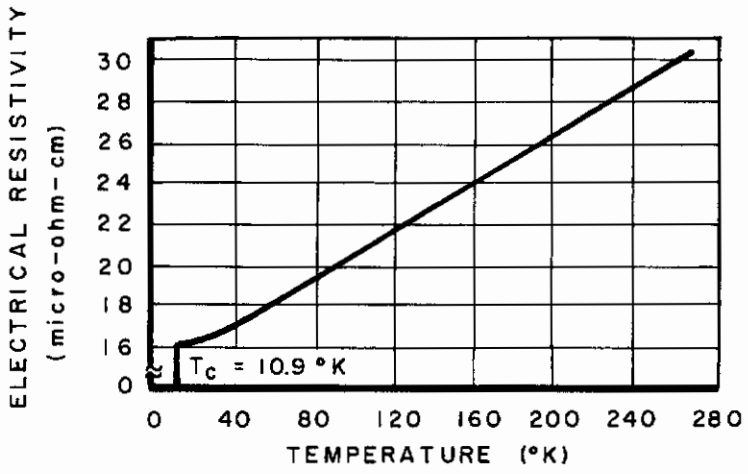


Figure 17. Electrical Resistivity vs. Temperature for Nb + 15% Zr Sample

Figure 18 shows the results for three different samples of Nb + 25% Zr cut from the same piece of wire. Although the values obtained are quite different for the three samples (variation is 4% between samples #1 and #3 at 273.2°K) the data do follow about the same type of curve. The three values of T_c vary by only 0.2°K but are below the reported value of about 10.9°K (Reference 2). For the curve drawn in Figure 18, ρ_o = 24.6 μ-ohm-cm and ρ_{T_3} = 37.9 μ-ohm-cm.

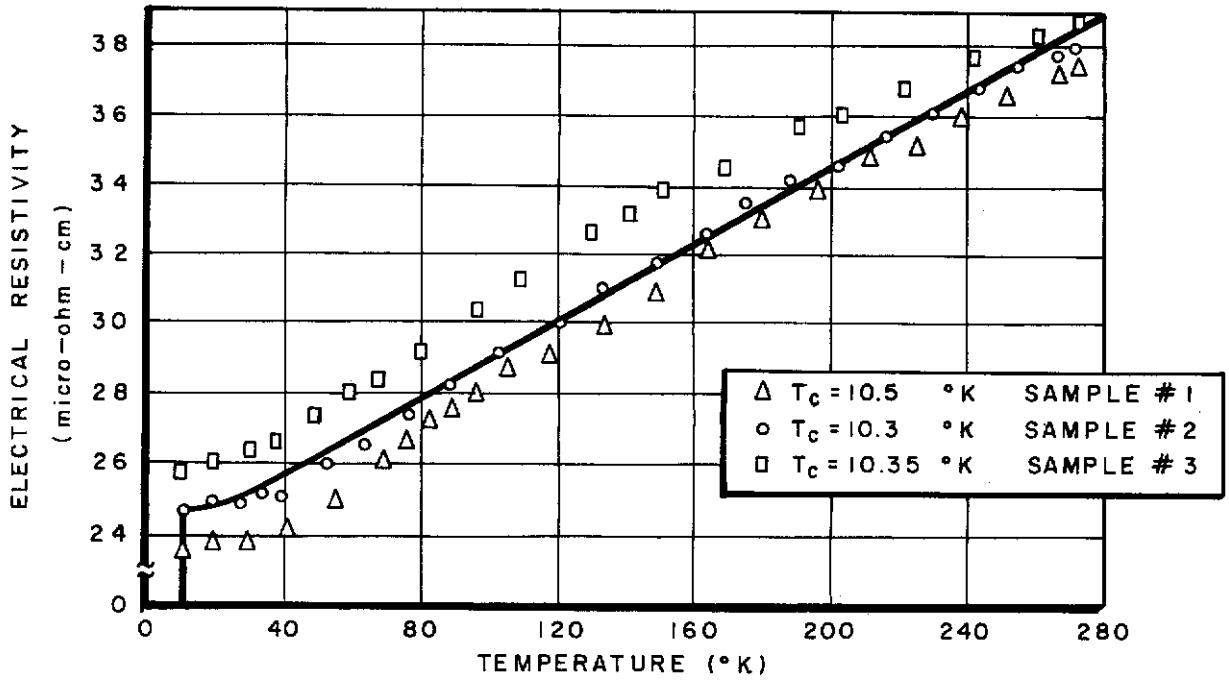


Figure 18. Electrical Resistivity vs. Temperature for Three Nb + 25% Zr Samples

Figure 19 shows a plot of electrical resistivity as a function of temperature for a Nb + 33% Zr sample. The T_c measured was 10.2°K as compared to a literature value of about 10.6°K. For this sample ρ_o = 31.4 μ-ohm-cm and ρ_{T_3} = 43.7 μ-ohm-cm.

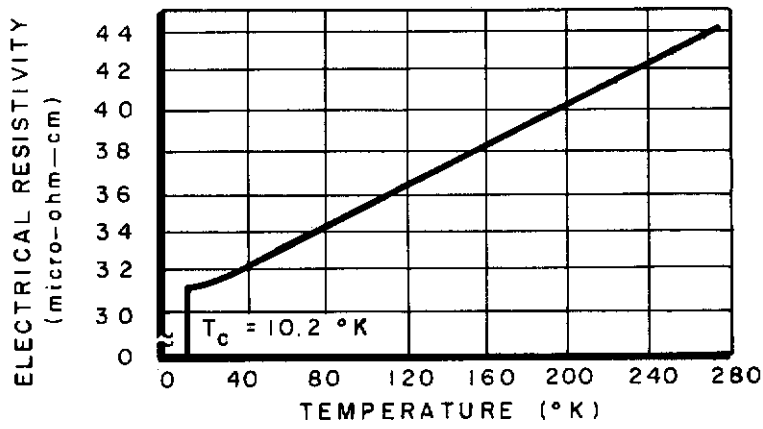


Figure 19. Electrical Resistivity vs. Temperature for Nb + 33% Zr Sample

Figure 20 gives the results of the data on two Nb + 50% Zr samples. For sample #1 the T_c measured was 9.65°K. This compares with a value of 9.6°K reported in the literature (Reference 2). For this sample ρ_o = 50.5 μ-ohm-cm and ρ_{T_3} = 61.7 μ-ohm-cm. The superconducting-normal transition was passed through three times for sample #2, and the values of T_c obtained were 10.1°K, 9.45°K, and 9.85°K for an average T_c of 9.8°K. For this sample ρ_o = 52.1 μ-ohm-cm and ρ_{T_3} = 63.6 μ-ohm-cm.

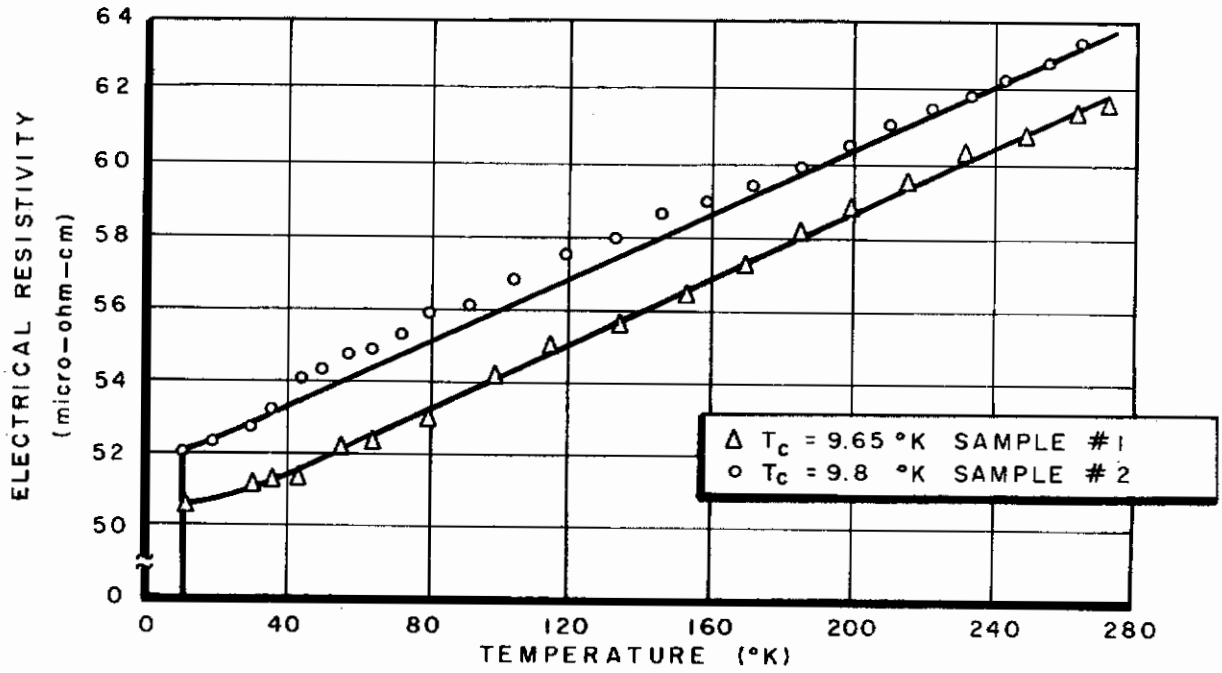


Figure 20. Electrical Resistivity vs. Temperature for Two Nb + 50% Zr Samples

Figure 21 shows all the data on the Nb and Nb-Zr samples plotted on one chart. From this chart, one can compare the slopes of the resistivity vs. temperature curves and the dependence of ρ_o on composition. Figure 22 shows values of the resistivity ratio plotted as a function of temperature for the same samples.

Figure 23 is a plot of electrical conductivity at 273.2°K as a function of zirconium concentration in volume percent. From the second rule of LeChatelier and Guertler (Reference 17) one would expect a U-shaped curve in the conductivity-composition diagram and this is the result obtained.

Assuming that the linear dependence of resistivity is correct, a least squares analysis was made of the data and the values of ρ_o' and α in the equation

$$\rho = \rho_o' + \alpha T \qquad (6)$$

were determined as were the root mean square deviation and the maximum absolute deviation. These values are listed in Table 3. The slopes of the resistivity vs. temperature curves vary by about 10 percent from Nb to Nb + 33% Zr. However, the slope

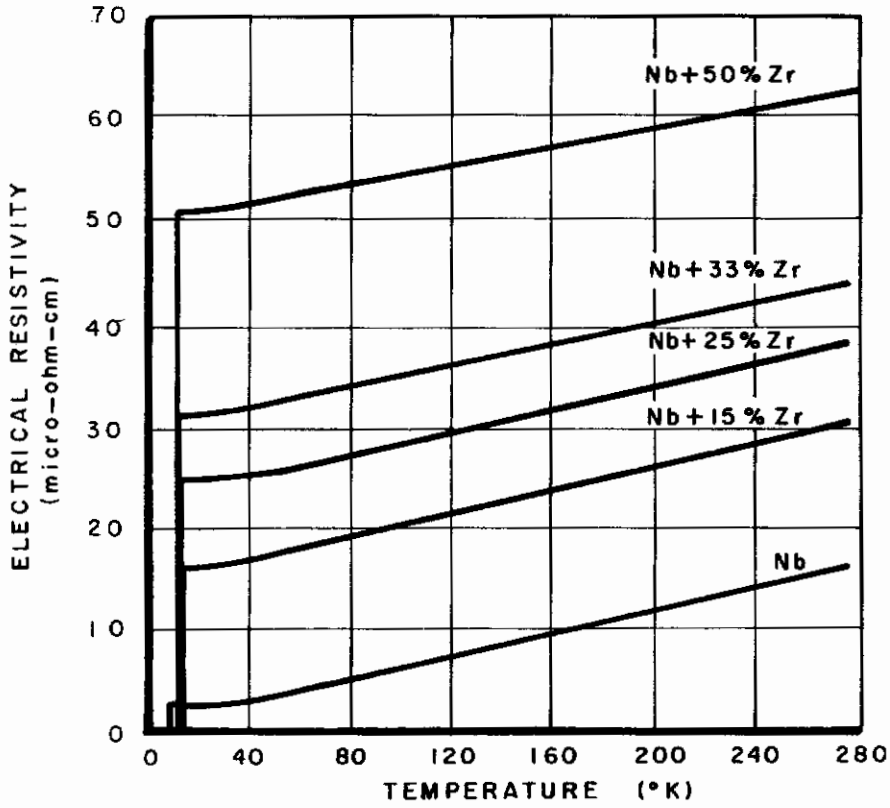


Figure 21. Electrical Resistivity vs. Temperature for Nb and Nb-Zr Alloys

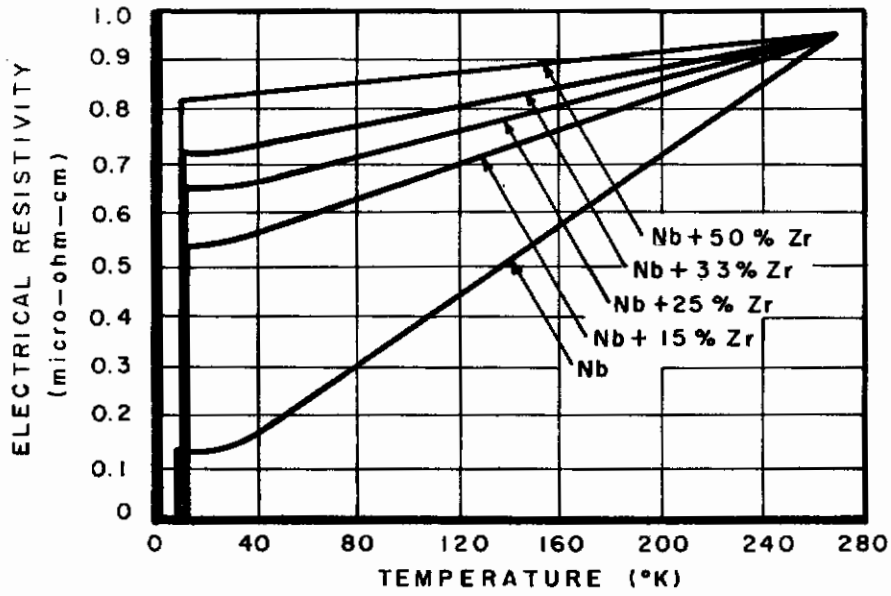


Figure 22. Resistivity Ratio vs. Temperature for Nb and Nb-Zr Alloys

of the Nb + 50% Zr curve varies by 25 percent from that of pure Nb. In an attempt to determine the dependence of the resistivity on zirconium concentration, values of ρ_o were plotted as a function of zirconium concentration as shown in Figure 24. The residual resistivity seems to depend linearly on composition for the 15, 25, and 33 percent alloys. However, the value for the 50 percent alloy does not fall on this line.

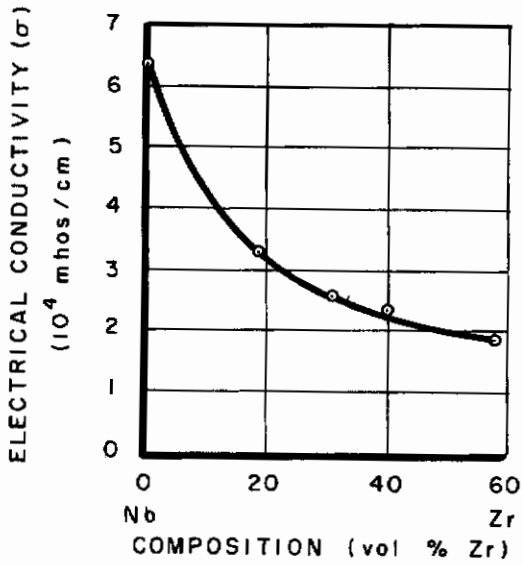


Figure 23. Electrical Conductivity vs. Zr Concentration

TABLE 3
RESULTS OF LEAST SQUARES ANALYSIS

SAMPLE	ρ'_o (μ-ohm-cm)	a (μ-ohm-cm/°K)	RMS DEVIATION (μ-ohm-cm)	MAX ABSOLUTE DEVIATION (μ-ohm-cm)
Nb	.16	.0587	.12	.24
Nb + 15% Zr	14.8	.05799	.14	.31
Nb + 25% Zr #1	22.18	.05807	.29	.54
#2	23.13	.05642	.22	.48
#3	24.91	.05417	.39	.76
Nb + 33% Zr	30.25	.05377	.12	.25
Nb + 50% Zr #1	49.54	.04570	.15	.30
#2	52.11	.04251	.23	.57

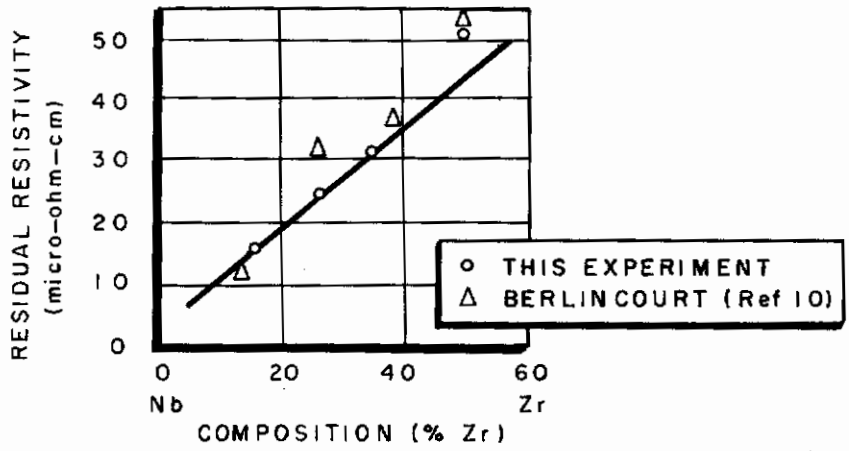


Figure 24. Residual Resistivity vs. Zr Concentration

CONCLUSIONS

The electrical resistivity of Nb-Zr alloys of four compositions has been determined as a function of temperature from 4.2°K to 273.2°K. The estimated accuracy of the resistivity measurement is 4 percent and the temperature measurement is accurate to 1°K. The critical temperature of these alloys was also measured to an estimated accuracy of ±0.5°K.

The temperature dependence of the electrical resistivity was found to be very nearly linear, and, with the exception of the Nb + 50 percent Zr sample, the data were found to be in approximate agreement with Matthiessen's Rule. As was mentioned previously, the applicability of Matthiessen's Rule to alloys is questionable for concentrations of solute metals exceeding 5 percent. In this case the concentration of solute metal varied from 15 to 50 percent. Thus, the fact that the 50 percent alloy does not agree with the results on the lower concentrations is not surprising. In addition, to apply this rule, the samples should be disordered so that ρ_o is temperature independent and they should also be single phase. No evidence showed any ordering of the lattice or the presence of a second phase. It is felt that the data obtained are in close enough agreement with Matthiessen's Rule to justify its use in explaining the results.

It was also found that the residual resistivity of the samples depends linearly on zirconium concentration except for the Nb + 50 percent Zr sample. The straight line in Figure 24 showing this dependence was drawn on the basis of the three lower compositions. That this may not be the correct line is shown by the data of Berlincourt and Hake (Reference 10) which is partially included on Figure 24. They had a greater number of samples with several compositions above 50 percent Zr which are not shown. Their published data show a linear dependence with the line passing through zero, through their 11.8 percent Zr data point and through their 50 percent Zr data point. Even though it should not make a significant difference, their data are normal resistivities at 1.2°K obtained by use of pulsed magnetic fields. The results of this experiment are generally in agreement with their results and the conclusion is drawn that the residual resistivity does depend linearly on zirconium concentration.

The data obtained during this investigation were compared with the Gruneisen-Borelius relation which states that for isotropic conducting metals the reduced resistance R_T/R_θ is a linear function of the reduced temperature T/θ where θ is the Debye temperature. The straight line

$$\frac{R_T}{R_\theta} = 1.17 \frac{T}{\theta} - 0.17 \qquad (7)$$

is a good approximation for the resistance of an isotropic metal in the region $0.2 < \frac{T}{\theta} < 1.2$. Deviations occur at the low and the high temperature extremes (Reference 17).

The data from the least squares analysis for the samples measured in this experiment were used to determine the reduced resistance and reduced temperature. Of course, only the temperature dependent portion of the total resistivity was used. The equation obtained for the Nb sample was $\rho_T/\rho_\theta = 1.16\ T/\theta - 0.16$ and that for the Nb + 15% Zr samples was $\rho_T/\rho_\theta = 1.11\ T/\theta - 0.11$. The data for all the other samples fell between these two lines, and no dependence on zirconium concentration could be resolved.

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