

wave, the reflection coefficient decreases monotonically to zero while the transmission coefficient increases monotonically to unity as  $-v_z/c$  approaches unity.

It is noted that the formulas for the reflection and the transmission coefficients may also be obtained by using the Fresnel formulas.<sup>4</sup>

<sup>4</sup> C. Møller, *The Theory of Relativity* (Oxford University Press, London, 1957), p. 209.

Similar techniques may be used to obtain the reflection and transmission coefficients of an incident  $H$  plane wave.

#### ACKNOWLEDGMENTS

I wish to thank Professor C. T. Tai for sending me his memo describing the topics to be presented in an URSI spring meeting, 1965, at Washington, D. C.

## Electrical Resistivity of Niobium-Zirconium Alloys below 273.2°K

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(Received 7 April 1965; in final form 30 June 1965)

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 was shown to depend linearly on zirconium concentration.

### 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 that they would carry high currents in high magnetic fields.<sup>1,2</sup> Superconducting Nb-Zr alloys have been found to have useful current densities at fields as high as 80 kG (for example:  $J_c > 10\,000$  A/cm<sup>2</sup> at 80 kG and 1.5°K).<sup>1</sup>

The upper critical field of Nb-Zr alloys increases with increasing zirconium concentration, reaches a maximum between 65 and 75 at.% zirconium, and then drops quite rapidly.<sup>3</sup> However, the maximum current carrying capacity in fields of interest increases with decreasing zirconium content, reaches a maximum at about 25%-35% zirconium, and falls rapidly at lower concentrations.<sup>1</sup> The critical temperature  $T_c$  increases with

increasing zirconium content, reaches a maximum at 20% Zr, and then slowly decreases.<sup>4</sup>

The phase diagram of Nb-Zr was published in 1955.<sup>5</sup> 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.<sup>2,6</sup> Work on the microstructure of Nb+25% Zr alloys has been reported by Walker, Stickler, and Werner.<sup>6,7</sup> 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.<sup>8</sup>

A compilation of the engineering properties of niobium and niobium alloys has been published, but this includes

\* This work is based in part on a thesis submitted by D. J. Evans to Ohio State University in partial fulfillment of the requirements for the degree Master of Science.

<sup>1</sup> J. E. Kunzler, *Rev. Mod. Phys.* **33**, 501 (1961).

<sup>2</sup> T. G. Berlincourt, R. R. Hake, and D. H. Leslie, *Phys. Rev. Letters* **6**, 671 (1961).

<sup>3</sup> T. G. Berlincourt and R. R. Hake, *Phys. Rev.* **131**, 140 (1963).

<sup>4</sup> J. K. Hulm and R. D. Blaugher, *Phys. Rev.* **123**, 1569 (1961).

<sup>5</sup> B. A. Rogers and D. F. Atkins, *J. Metals* **7**, 1034 (1955).

<sup>6</sup> *Superconductors*, edited by M. Tanenbaum and M. V. Wright (John Wiley & Sons, Inc., New York, 1962).

<sup>7</sup> *Metallurgy of Advanced Electronic Materials*, edited by G. E. Brock (John Wiley & Sons, Inc., New York, 1962).

<sup>8</sup> F. J. Morin and J. P. Maita, *Phys. Rev.* **129**, 1115 (1963).

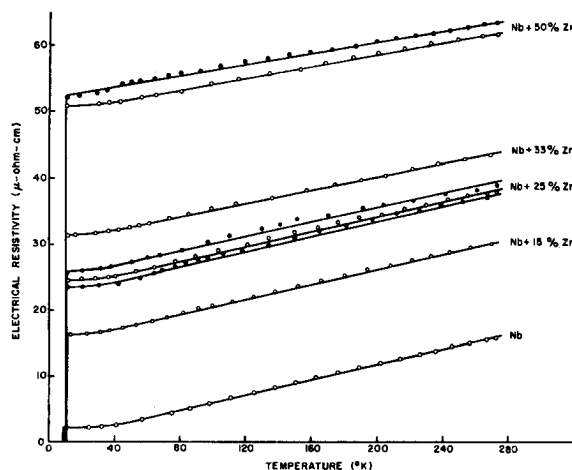


FIG. 1. Electrical resistivity as a function of temperature for Nb-Zr alloys.

only data on the Nb+1% Zr and Nb+5% Zr alloys.<sup>9</sup>

In a review of the literature, the only electrical resistivity data found were values at 300°, 273°, 195°, 77.3°, and 1.2°K.<sup>3,5,10</sup> This report is concerned with measuring the electrical resistivity of Nb-Zr alloys continuously from their transition temperatures ( $T_c$ ) up to 273.2°K ( $T_3$ ).

#### APPARATUS AND SAMPLES

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 was made of glass, was silvered except for one strip, and had a capacity of about 5 liters. A 5-mV full scale, 12 point recording potentiometer was chosen for recording all parameters except the voltage drop across the sample, and for this a 100- $\mu$ V full-scale recording potentiometer was used. In the temperature range 4.2°–100°K a germanium resistance thermometer was used as the temperature sensing element. In the range 77°–273.2°K a copper-constantan thermocouple was used. A four probe technique was used to make the resistivity measurements.

As a calibration of the apparatus, the dependence of resistance on temperature was determined for a platinum sample, and the absolute value of resistivity fell within the range of room temperature values given in

<sup>9</sup> F. F. Schmidt and H. R. Ogden, "The Engineering Properties of Columbium and Zirconium Alloys," Defense Metals Information Center Report No. 188, Battelle Memorial Institute, Columbus, Ohio, 6 September 1963).

<sup>10</sup> Standard Niobium-Zirconium Superconducting Wire," Technical Data Bulletin 53-161, Westinghouse Electric Corporation, May 1963).

Ref. 11. Values of  $\rho_T/\rho_{T_3}$  were determined from the resistivity measurements. Values of this ratio were also computed for a platinum resistance thermometer (PRT) which was calibrated by the National Bureau of Standards. The two sets of values were plotted as a function of temperature from 80° to 300°K, and from this plot the accuracy of the resistivity measurement was determined on the assumption that the temperature measurement was correct. The largest deviation from the NBS data occurred at about 150°K and was 4%.

The temperature was checked in several ways. The germanium resistance thermometer (GRT) was calibrated from 1.5° to 100°K by the manufacturer, and it is very sensitive especially at the lower temperatures. 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 up to 100°K.

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

As a check of 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° to 246°K using this technique. The resistance of the PRT was measured with a Mueller bridge. The thermocouple output was recorded on the 5-mV recorder in the same manner in which it was done during actual experiments. The temperature differences between the PRT and the thermocouple were generally less than 0.5°K.

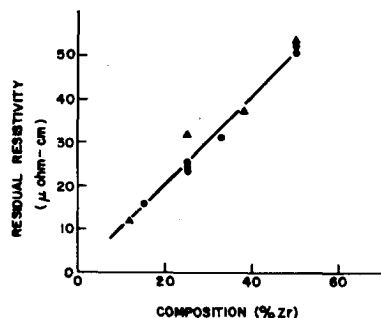
Considering (1) the values of resistivity at 273.2°K for Pt and Nb, (2) the values of resistivity at room temperature for Nb-Zr alloys as reported by Rogers and Atkins,<sup>5</sup> (3) the values of resistivity for Nb+25% Zr alloys given by Westinghouse for three different temperatures,<sup>10</sup> and (4) the values of resistivity ratios for

TABLE I. Values of residual resistivity, resistivity at 273.2°K, and critical temperature for Nb and Nb-Zr alloys.

Sample	$\rho_0$ ( $\mu\Omega\cdot\text{cm}$ )	$\rho_{T_3}$ ( $\mu\Omega\cdot\text{cm}$ )	$T_c$ (°K)
Nb	2.2	16.2	8.35
Nb+15% Zr	16.0	30.6	10.35
Nb+25% Zr # 1	23.6	38.0	10.5
# 2	24.6	38.5	10.3
# 3	25.7	39.7	10.35
Nb+33% Zr	31.4	44.9	10.2
Nb+50% Zr # 1	50.5	62.0	9.65
# 2	52.1	63.7	9.8

<sup>11</sup> N. Fuschillo and R. A. Lindberg, *Electrical Conductors At Elevated Temperatures*, ASD-TDR-62-481, January 1963.

FIG. 2. Residual electrical resistivity as a function of Zr concentration. The data of Berlincourt and Hake are given by the triangular points. The solid line is a least-squares fit to our data which are given by the circular points.



Pt, gives an estimated accuracy of the resistivity measurement of 4%.

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.

The Nb-Zr samples tested in this investigation were supplied by Westinghouse and were of the following compositions: Nb+15 wt% Zr, Nb+25% Zr, Nb+33% Zr, and Nb+50% Zr. These compositions vary by  $\pm 1\%$  Zr along the length and/or along a radius of the wire. The samples were in bare wire form of the following diameters (inches): 0.015 for the 15% Zr and 25% Zr, 0.0075 for the 33% Zr, and 0.0098 for the 50% Zr. The samples were  $1\frac{1}{2}$ -in. long. These alloys were analyzed using x-ray diffraction to determine the lattice constants. Values of the lattice constant obtained were 3.345, 3.368, 3.385, and 3.435 Å for the 15% Zr, 25% Zr, 33% Zr, and 50% Zr samples, respectively, showing that the lattice parameter varies linearly with composition in agreement with Vegard's law.

The Nb sample was obtained from a roll of 0.0249-in. wire and its source is not known. Spectrographic analysis of the 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 0.016-in. 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 RESULTS

The results of the measurements made on the Nb and the Nb-Zr samples are shown graphically in Fig. 1. The curves drawn on the resistivity vs temperature graph are straight line approximations except for the leveling out at the low temperature end. For all samples, a smooth curve through the data points would be slightly concave downward. Table I lists the data obtained. The residual resistivity ( $\rho_0$ ) was found by extrapolating the curves in Fig. 1 to 0°K. The values of the electrical resistivity at 273.2°K ( $\rho_{T_3}$ ) were calculated from least-squares analyses of the data. For several of the samples the superconducting-normal

transition was passed through three times and for these cases the  $T_c$  listed is the average value. For the two instances in which more than one sample of a given composition is listed, the results are for different samples cut from the same piece of wire.

A least-squares fit of the data above 35°K to the approximate form  $\rho = \rho_0' + \alpha T$  was made and the corresponding values of  $\rho_0'$  and  $\alpha$  are listed in Table II along with values for the root mean square deviation and the maximum absolute deviation. The slopes of the linear approximations vary by about 10% from Nb to Nb+33% Zr. However, the slope of the Nb+50% Zr curve varies by 25% from that of pure Nb. Values of  $\rho_0$  are plotted as functions of zirconium concentration in Fig. 2. The residual resistivity seems to depend linearly on composition for these alloys.

## CONCLUSIONS

The electrical resistivities of Nb-Zr alloys of four compositions have been determined as functions of temperature from 4.2° to 273.2°K. The estimated accuracy of the resistivity measurement is 4%, and the temperature measurement is accurate to 1°K. The critical temperatures of these alloys were also measured to an estimated accuracy of  $\pm 0.5^\circ\text{K}$ .

The temperature dependence of the electrical resistivity between 35° and 273.2°K was found to be approximately linear, and, with the exception of the Nb+50% Zr sample, the data were found to be in approximate agreement with Matthiessen's rule.<sup>12</sup> The applicability of Matthiessen's rule to alloys is questionable for concentrations of solute metals exceeding 5%, and in this case the concentration of solute metal varied from 15% to 50%. Thus, the fact that the 50% alloy does not agree with the results on the lower concentrations is not surprising. In addition, for this rule to be applicable, the samples should all be of the same phase. No evidence showed any ordering of the lattice or the presence of a

TABLE II. Results of least-squares analyses to fit data to the linear equation  $\rho = \rho_0' + \alpha T$ .

Sample	$\rho_0'$ ( $\mu\Omega \cdot \text{cm}$ )	$\alpha$ ( $\mu\Omega \cdot \text{cm}/^\circ\text{K}$ )	rms deviation ( $\mu\Omega \cdot \text{cm}$ )	Max. absolute deviation ( $\mu\Omega \cdot \text{cm}$ )
Nb	0.16	0.0587	0.12	0.24
Nb+15% Zr	14.8	0.05799	0.14	0.31
Nb+25% Zr # 1	22.18	0.05807	0.29	0.54
# 2	23.13	0.05642	0.22	0.48
# 3	24.91	0.05417	0.39	0.76
Nb+33% Zr	30.25	0.05377	0.12	0.25
Nb+50% Zr # 1	49.54	0.04570	0.15	0.30
# 2	52.11	0.04251	0.23	0.57

<sup>12</sup> N. F. Mott and H. Jones, *The Theory of The Properties of Metals and Alloys* (Clarendon Press, Oxford, 1936).

second phase. It is felt that the data obtained are in close enough agreement with Matthiessen's rule to justify its use in describing the results.

It was also found that the residual resistivity of the samples depends linearly on zirconium concentration as shown in Fig. 2. Also shown are the results reported by Berlincourt and Hake<sup>3</sup> in this same composition range. The data were fitted by the method of least squares to the line  $\rho_0 = \rho_0^0 + \beta C$  where  $C$  is the zirconium concentration in percent. The line drawn on Fig. 2 was fitted to our data and has parameters  $\rho_0^0 = -0.2 \mu\Omega \cdot \text{cm}$  and  $\beta = 1.009 \mu\Omega \cdot \text{cm}/\%$  Zr. A line fitted to all of the data shown in Fig. 2 would have parameters  $\rho_0^0 = -0.08 \mu\Omega \cdot \text{cm}$  and  $\beta = 1.017 \mu\Omega \cdot \text{cm}/\%$  Zr.

The data obtained during this investigation were compared with the Gruneisen-Borelius relation which states that over a certain temperature range for isotropic conducting metals the reduced resistance  $R_T/R_\theta$  is a linear function of the reduced temperature  $T/\theta$  where

$\theta$  is the Debye temperature. The straight line  $R_T/R_\theta = 1.17(T/\theta) - 0.17$  is a good approximation for the resistance of an isotropic metal in the region  $0.2 < T/\theta < 1.2$ . Deviations occur at the low and the high temperature extremes.<sup>13</sup>

The data from the least-squares analyses 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 values of  $\theta$  were interpolated from the data of Morin and Maita.<sup>8</sup> The equation obtained for the Nb sample was  $R_T/R_\theta = 1.16(T/\theta) - 0.16$  and that for the Nb+15% Zr sample was  $R_T/R_\theta = 1.11(T/\theta) - 0.11$ . The data for all the other samples fell between these two lines, and no dependence on zirconium concentration could be resolved.

<sup>13</sup> A. N. Gerritsen, "Metallic Conductivity" in *Encyclopedia of Physics*, edited by S. Flugge (Springer-Verlag, Berlin, 1956), Vol. XIX.

## Effect of Surface Pinning on the Magnetization of Thin Films\*

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(Received 16 December 1964)

The effect of surface pinning, as manifested by a surface anisotropy field, on the magnetization of thin films is examined in detail for a simple cubic lattice of atoms having spin  $\frac{1}{2}$  coupled by pure exchange. The magnetization-versus-temperature curve is found to lie above that obtained in the absence of pinning. For very weak pinning (surface anisotropy field much less than surface exchange field), the magnetization is sensitive to film thickness falling off more rapidly than for bulk, in qualitative agreement with some experiments. For intermediate pinning, the magnetization is essentially independent of film thickness, following the bulk behavior, in qualitative agreement with other experiments. For very strong pinning (surface anisotropy field on the order of or greater than surface exchange field), the magnetization falls off slower than for bulk, again with a thickness dependence. As a consequence, one may interpret experimental results in terms of the degree of surface spin pinning. Physically it is not yet clear why the degree of pinning should behave in the required fashion.

### I. INTRODUCTION

THE experimental behavior, at low temperatures, of the magnetization of a thin ferromagnetic film is such that the magnetization temperature relationship in some cases is essentially the same as for a bulk sample, and in other cases is sensitive to the film thickness, falling off much more rapidly than for a bulk sample. Experimentally it is not clear why this situation prevails. Initial experimental evidence,<sup>1-5</sup> obtained by

utilizing various experimental techniques, indicated that the magnetization is strongly dependent on thickness. Perhaps best known are the hysteresis loop measurements of Crittenden and R. W. Hoffman.<sup>2</sup> However, the more recent torque measurements of Neugebauer<sup>6</sup> performed under ultrahigh vacuum (unlike Crittenden and R. W. Hoffman) and the high-vacuum hysteresis measurements of H. Hoffmann<sup>7</sup> show no thickness dependence for films down to roughly 20 Å. Neugebauer and H. Hoffmann both observe a drop in the magnetization as air is admitted. Subsequent experiments by Gondo, Konno, and Funato-

\* Work supported by the U. S. Air Force Office of Scientific Research, under Grant No. AF 196-63.

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<sup>6</sup> C. A. Neugebauer, *Phys. Rev.* **116**, 1441 (1959); *Z. Angew. Phys.* **14**, 182 (1962).

<sup>7</sup> H. Hoffmann, *Z. Angew. Phys.* **13**, 149 (1961).