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PRELIMINARY OBSERVATIONS OF THE ENHANCEMENT OF SUPERCONDUCTING CURRENT-CARRYING CAPACITY IN NIOBIUM THROUGH HYDROGEN TREATMENT

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PRELIMINARY OBSERVATIONS OF THE ENHANCEMENT OF SUPERCONDUCTING CURRENT-CARRYING CAPACITY IN NIOBIUM THROUGH HYDROGEN TREATMENT

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SUMMARY

Measurements of resistivity as a function of applied magnetic field at constant current and temperature and resistivity as a function of temperature at constant current and field were obtained for niobium below 20° K. The measurements were taken after annealing niobium at 1600° C and again after treating the annealed niobium with hydrogen in a 0.1 N sulfuric acid solution. The results show that the current-carrying capacity of the hydrogen-treated niobium is greater than four times that of annealed niobium.

INTRODUCTION

The presence of lattice defects caused by impurities, work hardening, heat treating, or irradiation can raise the current-carrying capacity of a hard superconductor (ref. 1). Increases of the current-carrying capacity can be as large as a factor of four for several pure metals and an order of magnitude for several high-field alloys (refs. 2 and 3). DeSorbo (ref. 4) reported that unannealed and outgassed niobium has a higher current-carrying capacity than annealed niobium. In studies of palladium (ref. 5), it was observed that the slope of the resistivity against temperature (ρ against T) curve, the thermoelectric power values, and the lattice constant (taken by X-ray diffraction) were altered as a result of the absorption and desorption of hydrogen. It was suggested that these changes were caused by residual imperfections in the lattice. Niobium (ref. 6) and palladium (ref. 7) absorb hydrogen up to a hydrogen-metal atom ratio of at least 0.7, and the lattice constants of both increase as a result of this absorption. The absorption and desorption of hydrogen might produce defects in niobium, as was suggested for palladium. If defects are produced in the niobium lattice, an increase in its current-carrying capacity in the superconducting state might be observed.

SYMBOLS

H	applied magnetic field, Oe
I	sample current, mA
T	temperature, $^{\circ}K$
T_c	transition temperature, $^{\circ}K$
ρ	resistivity of niobium sample after annealing, $\mu\Omega$-cm
ρ'	resistivity of niobium sample after hydrogen treatment, $\mu\Omega$-cm
ρ_0	normal state resistivity of annealed niobium immediately above T_c, $\mu\Omega$-cm
ρ_0'	normal state resistivity of hydrogen-treated niobium immediately above T_c, $\mu\Omega$-cm

EXPERIMENTAL

A 0.0254-centimeter-diameter, 99.7-atomic-percent niobium wire (major impurity molybdenum) was used in this experiment. The wire was spotwelded to the specimen holder as shown in figure 1. The specimen holder itself comprised the current leads. Niobium potential leads were spotwelded to the specimen with a 2.20-centimeter spacing. The sample was annealed by Joule heating at 1600° C for 30 minutes at 10^{-7} torr. The heating current through the sample was reduced to zero over a 2-minute period. A germanium resistance thermometer was then attached to the center of the sample.

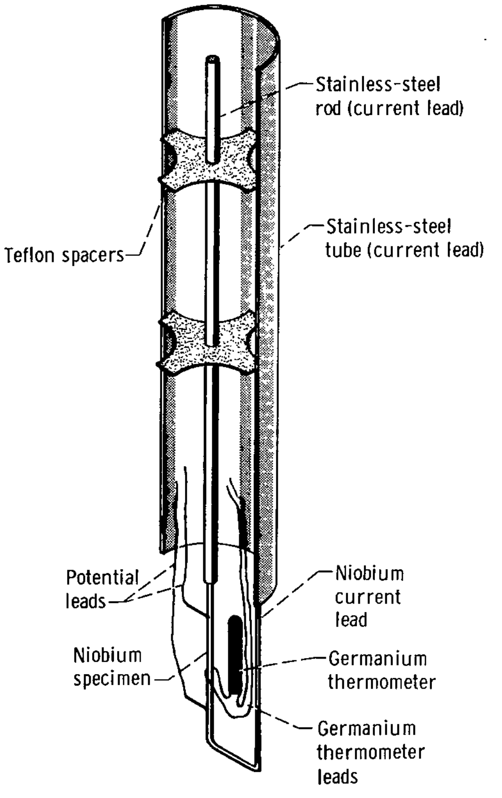


Figure 1. - Specimen holder with specimen and thermometer before insertion into heat leak can.

The resistivity was measured with H held constant at 0, 1, and 3 kilooersteds; I held constant at 50, 100, and 200 milliamperes; and T varied from 5° to 10° K for all combinations of H and I. The resistivity was then measured with I held constant at 50, 100, and 200 milliamperes; T held constant at 5.987° K; and H varied from 0 to 15 kilooersteds for each value of I. Sample purity and the uncertainties in the

TABLE I. - SAMPLE PURITY AND UNCERTAINTIES IN DATA

Sample purity	99.7 percent; molybdenum major impurity; Tantalum $\simeq$ 100 ppm; total additional impurity $<$ 100 ppm
Applied magnetic field, H	±3 percent error at 100 Oe ±0.5 percent error at 500 Oe ±0.2 percent error at 1 kOe and above
Temperature, T	±0.15 percent of T error (overall accuracy of the measurement) or $\pm 0.01^{\circ}$ K error (swing in temperature due to on-off cycling of temperature controller)
Sample current, I	±1 part error in 10^5
Computation of ρ (or ρ') from potential drop, cross-sectional area, and potential lead spacing	Diameter of wire, 0.0254±0.0001 cm; potential lead spacing, 2.20 cm

data are presented in table I.

A gas analysis performed subsequent to the measurements indicated a total gas content of less than 100 ppm. The final hydrogen concentration was similar to that of the annealed specimen.

The magnetoresistance of the germanium thermometer did not affect the temperature readings until the field exceeded 9 kiloersteds; hence, the temperature values in fields less than 9 kiloersteds are correct within the accuracy of the instrumentation in zero field application. Above 9 kiloersteds the magnetoresistance of the thermometer results in an uncertainty in T; however, since the conclusions herein are based on data taken in fields of less than 9 kiloersteds, this error is ignored.

Hydrogen absorption was accomplished electrolytically at room temperature. After all specimen leads had been coated with paraffin, so that only the section of the niobium between the potential leads was exposed, the specimen was placed in a 0.1 N sulfuric acid solution. With platinum as the anode and the niobium as the cathode, a 5-milliampere current was passed through the solution for 21 hours.

After charging with hydrogen, the sample was returned to the Dewar and two room-temperature measurements of ρ' were made to check the stability of the hydrogen concentration. These measurements were made 5 and $7\frac{1}{2}$ hours after the specimen had been removed from the acid solution. After completion of the ρ' measurements, the sample was removed from the Dewar and a section of the sample between the potential leads was analyzed for hydrogen content by mass spectroscopy.

RESULTS

In the normal state, the resistivity of the niobium wire was independent of the currents and magnetic fields used in this experiment.

During the interval between the two room temperature measurements ρ' decreased by 0.2 percent. This decrease was not unexpected, since similarly treated specimens exhibited decreases in hydrogen concentration from a hydrogen-niobium atom ratio of 0.2 (immediately after charging) to approximately 0.04 in 4 hours. The low-temperature measurements were started 24 hours after removal from the acid solution, and ρ'_0 was observed to be approximately 9 percent greater than ρ_0 (when compared at the same temperature). At the end of the measurement period (15 days later), however, ρ'_0 was only 6.6 percent greater than ρ_0. The final hydrogen content was determined after the completion of the ρ' measurements, and the hydrogen-niobium atom ratio was approximately 0.004, which is in the range of the as-received niobium (0.002 to 0.006).

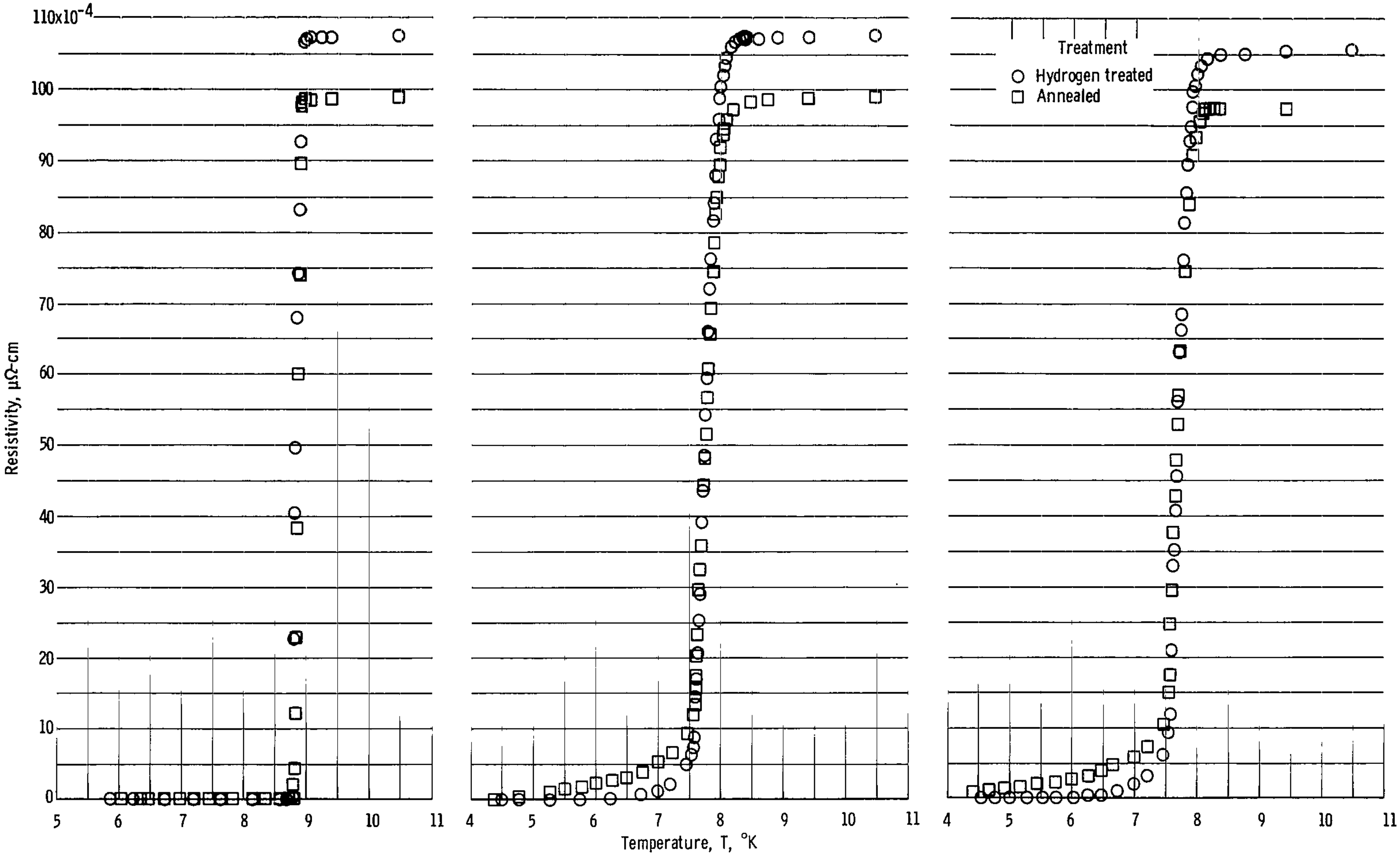
The resistivity data are plotted in figures 2 and 3. These curves indicate that the superconducting state persists to higher fields and temperatures after hydrogen treatment.

In all cases of electrolytic hydrogen absorption up to a hydrogen-niobium atom ratio of 0.45, the niobium wire remained malleable, although the hardness did increase somewhat. All the absorption efforts in a hydrogen gas atmosphere at elevated temperatures resulted in embrittled wire. The reasons for this disparity are now under investigation.

DISCUSSION

Since it was determined that niobium may lose most of the absorbed hydrogen in the first few hours after removal from the electrolytic bath, the observed decrease of ρ' and ρ'_0 with time is attributed to continued hydrogen desorption. In this case, it is assumed that the hydrogen acts as an additional scattering center and that ρ' and ρ'_0 decrease with hydrogen desorption. Previous residual effects observed in palladium, however, suggest that some stable defects remain in the niobium lattice after the hydrogen is disorbed. These defects are probably responsible for the increase in current-carrying capacity observed in this experiment.

While the actual hydrogen-niobium atom ratio was not known, it is estimated that the ratio was less than 0.04 for most ρ' measurements. This estimate is based on the previously mentioned hydrogen loss rate. Moreover, the low ratio is consistent with the fact that there was no measurable change in the temperature or field at which the sample became completely normal. This explanation is based on the work of DeSorbo (ref. 4), who reported that the addition of hydrogen to niobium (atom ratio, 0.04) results in a

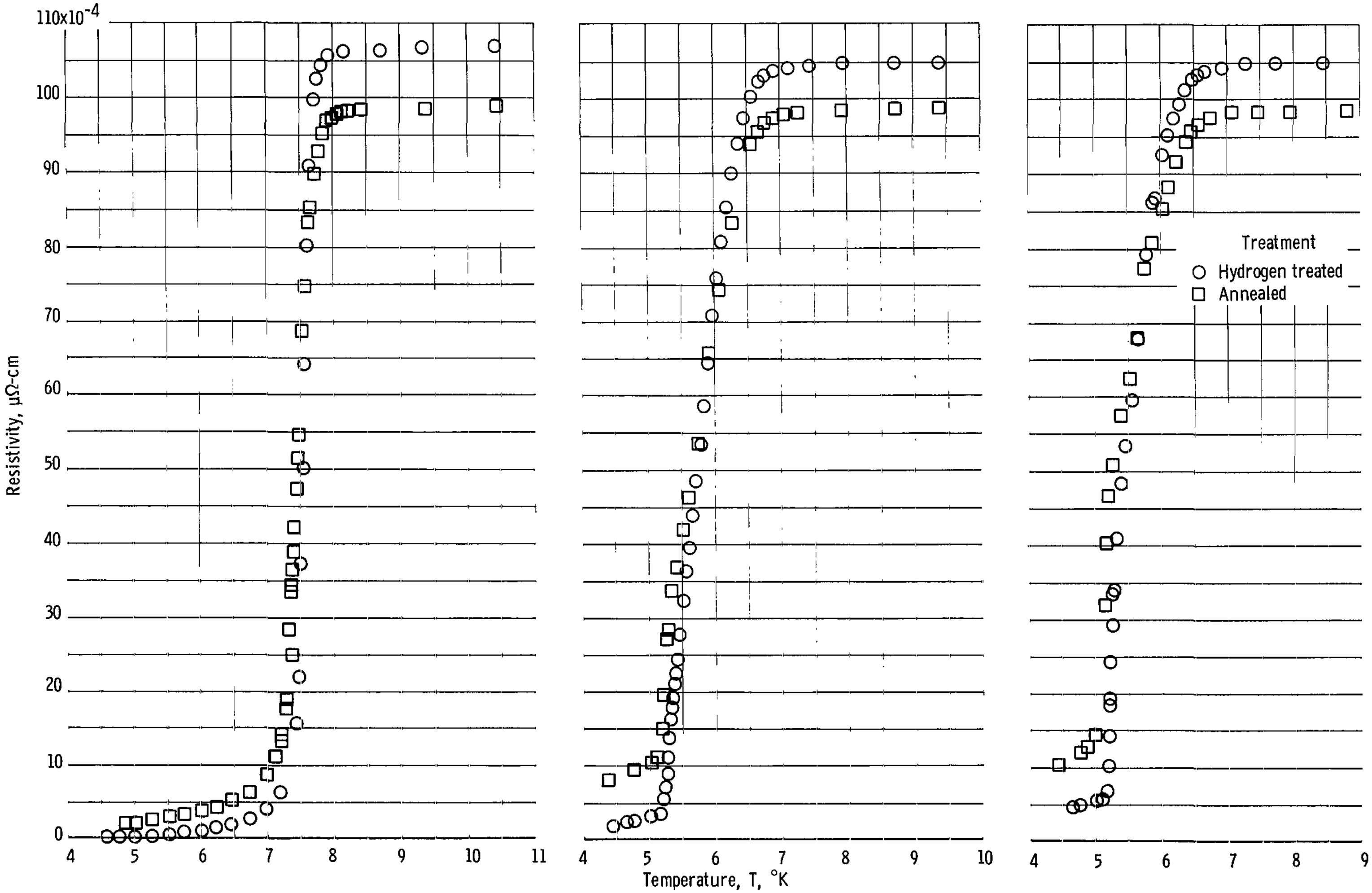


(a) Sample current, 50 milliamperes; magnetic field, 0 kiloersted.

(b) Sample current, 50 milliamperes; magnetic field, 1 kiloersted.

(c) Sample current, 100 milliamperes; magnetic field, 1 kiloersted.

Figure 2. - Variation of resistivity of niobium as a function of temperature.

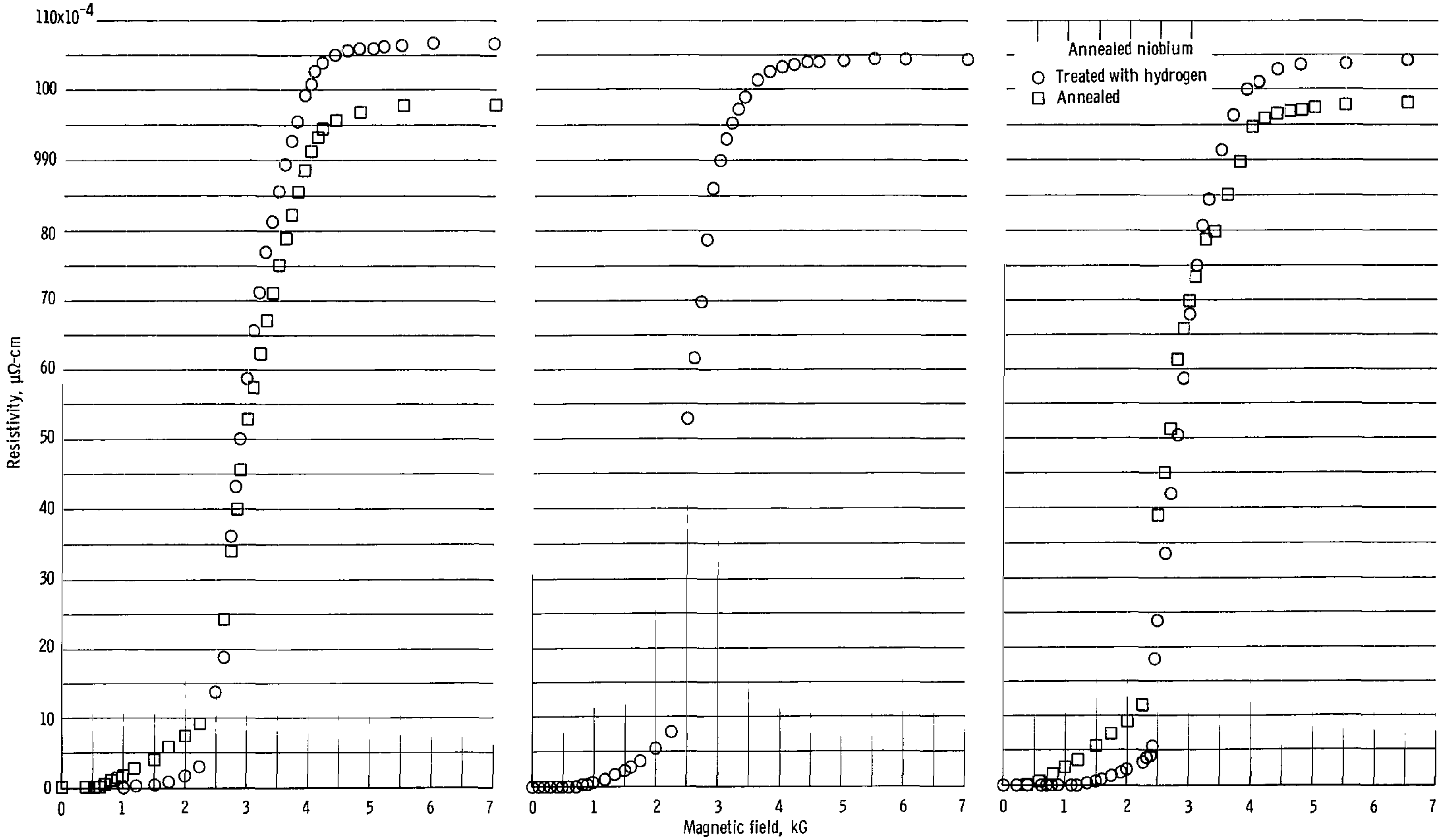


(d) Sample current, 200 milliamperes; magnetic field, 1 kiloersted.

(e) Sample current, 100 milliamperes; magnetic field, 3 kiloersteds.

(f) Sample current, 200 milliamperes; magnetic field, 3 kiloersteds.

Figure 2. - Concluded.



(a) Sample current, 50 milliamperes.

(b) Sample current, 200 milliamperes.

(c) Sample current, 100 milliamperes.

Figure 3. - Variation of resistivity of niobium as function of magnetic field at constant temperature of 5.987° K.

TABLE II. - RESISTIVITY OF ANNEALED NIOBIUM AT CONSTANT TEMPERATURE

[Temperature, 5.987° K.]

Temperature, T, °K	Annealed niobium; sample current, 50 mA	Hydrogen-treated niobium; sample current, 200 mA
	Resistivity, $\mu\Omega$-cm	
0.7	0.3	0
1.0	0.75	0.35
1.5	1.85	1.15
2.0	3.25	2.25
2.25	4.0	3.5

TABLE III. - RESISTIVITY OF ANNEALED NIOBIUM AT CONSTANT FIELD

[Magnetic field, 1 kOe.]

Temperature, T, °K	Annealed niobium; sample current, 50 mA	Hydrogen-treated niobium; sample current, 200 mA
	Resistivity, $\mu\Omega$-cm	
5.0	0.22	0
5.5	0.50	0.1
6.0	0.90	0.3
6.5	1.30	0.7
7.0	2.30	1.6

decrease of the resistive transition temperature T_c in zero applied field from 9.46° to 9.2° K.

The transitions of the hydrogen-treated niobium from the superconducting to the normal state were sharper than those of the annealed niobium in all cases (figs. 2 and 3). Moreover, the superconducting state persisted to higher fields and temperatures in the hydrogen-treated niobium than in the annealed niobium. This indicates that the current-carrying capacity in the superconducting state is greater in the hydrogen-treated niobium than in the annealed niobium.

In fact, the superconducting current-carrying capacity of hydrogen-treated niobium is at least four times that of annealed niobium. This is indicated by the first entry of table II where ρ' is still zero (I = 200 mA) while ρ is 0.22 (I = 50 mA). The remainder of table II indicates that the electrical conductivity of hydrogen-treated niobium is greater than that of annealed niobium, at least up to 7° K. Similarly, the data in table III indicate that the electrical conductivity of hydrogen-treated niobium is greater than that of annealed niobium, at least up to 2.25 kiloersteds.

From the results obtained in this experiment, it appears that the current-carrying capacity of niobium can be increased by the creation of lattice defects through hydrogen treatment. The absorption is accompanied by a lattice expansion, and while the lattice constant may return to its original value after desorption, it is reasonable to assume that residual strains or defects remain in the lattice because of this process. An increase in impurity concentration would also cause $\rho'_0 > \rho_0$; however, there is no apparent reason to believe that the impurity concentration changed. The fact that it is possible to accomplish this absorption and desorption at room temperature implies that a relatively simple procedure for defect production is available for some superconducting materials. Apparently some control may be exercised over the quantity of defect by monitoring the absorption with resistance measurements and gas analysis.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, June 30, 1966,
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