Effects of High Temperature Vacuum Baking on Surface Oxides and the Transition Temperature of Niobium

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Abstract

Typical superconducting radio frequency cavities are manufactured from high-purity niobium because of its availability in pure form, malleability, thermal conductivity, and high transition temperature. The objective of this experiment is to look for minor changes in the transition temperature of niobium samples by absorbing surface oxide layers through vacuum baking at 140°C. The method is based on the Meissner effect where, in this study, a thin sheet of niobium is placed between an ac driven solenoid generating a magnetic field and a passive solenoid with a magnetically induced ac electromotive force. Temperature and voltage readings are electronically collected at fractional second intervals as the sample is thermally cycled above and below its transition temperature. The study showed that the transition temperatures of the heat-treated niobium samples actually decreased by a very small fraction of a degree (on the order of 0.05 K). The slope of the superconducting transition (voltage vs. temperature) curve also decreased, similar to the transition curve characteristic of an impure sample. The lower transition temperature and decreased slope can be accounted for by considering edge effects. The orientation of the magnetic field relative to the sample and the surface area of the sample make for a low magnetic shielding efficiency when the sample is in the superconducting state. The major result is that diffused oxygen from the 48-hour vacuum bake lowered the sample transition temperature by a small fraction of a degree. This allowed more magnetic flux to penetrate the sample until the lower transition temperature was reached, consequently degrading the slope of the transition to the superconducting state.

Introduction

The discovery of superconductivity by Kammerlingh Onnes in 1911 ushered in a new era for scientific advancement. He observed many strange phenomena that immediately showed potential for practical use. With the theoretical understanding of Bardeen, Cooper, and Schrieffer, the BCS theory, as it is called, became the leading model capable of explaining most of the mechanisms behind this marvelous discovery. Their theory attempts to make clear how the electrons (fermions) in the material condense to form pairs (making them bosons) with one another via electron-phonon interactions, so that they may exhibit new physical properties as pairs (now bosons) which they ordinarily would not possess. Superconductivity is characterized by many important experimental observations. Among the most important are zero surface resistances and complete magnetic flux exclusion. A significant fact about superconductors is that any direct current flowing through them will travel with no resistance. The case is similar, but not perfect, for alternating currents; because the

current is alternating back and forth there arises some residual resistance due to the electric fields acting on the inertial mass of the charge carriers (this effect is obviously greater at higher frequencies). Magnetic flux exclusion is another very important property of superconductors. Named the Meissner effect, after one of its discoverers, this magnetic flux exclusion is a direct consequence of the other extraordinary properties of a superconductor. The Meissner effect occurs once the superconductor reaches its transition temperature, the temperature at which the material becomes superconducting, at which time all magnetic flux within the superconductor is immediately pushed out so that there is no internal flux.

In recent years the physics of superconducting materials have made significant advances. With the advent of modern technology scientists from all disciplines have been given the opportunity to greatly improve their research tools and techniques. This has proven to be invaluable to many areas of science beyond physics: superconducting magnets have replaced normal magnets, the medical industry has incorporated superconducting materials into their magnetic resonance imagine equipment, and even the transportation industry has experimented with using superconducting materials for magnetic levitation. Within physics, however, the many advances superconductivity has given to experimental high-energy particle physics are remarkable.

High-energy particle accelerators have long been considered a marvelous technological innovation. At the heart of these complex machines is the mechanical element that makes high beam velocities and high beam currents possible: the accelerator. In modern particle accelerators, this distinction is given to superconducting radio frequency cavities. These microwave resonance cavities are made from superconducting materials because of their unique properties at cryogenic temperatures. An understanding of the physics of superconductivity is thus important for improving cavity power loss, maximum accelerating gradient, and overall operating efficiency. Before superconductivity was discovered particle accelerator facilities were limited to using normal conducting (copper) radio frequency cavities to introduce energy to the particle beam. The effectiveness of these resonating electromagnetic cavities depends heavily on their quality factor. Large amounts of power are dissipated in the walls of these normal conducting cavities, and as a result, the quality factor of the cavity, being inversely proportional to the power lost, is significantly lowered. Superconducting radio frequency cavities have the advantage of having much lower surface resistances that substantially reduce the amount of power lost.

Recently, it has been discovered that vacuum baking of superconducting niobium cavities significantly improves cavity performance (this is the motivation behind this study). After vacuum baking both the degradation of the quality factor at high accelerating field gradients and the surface resistance are greatly reduced. The reason for the improvement of these cavity characteristics is not yet fully understood. The improvement of the superconducting properties of the cavity could be explained if the transition temperature of the cavity was higher after the bake. Thus we would like to know if the 140°C vacuum bake raises the transition temperature of the cavity.

Materials and Methods

Niobium

With the physical appearance of steel and the ductility of lead, niobium is a transi-

tion metal belonging to group 5B in the periodic table (Niobium-93 being the only natural isotope). Niobium has many chemical and physical properties that make it ideal for use in superconducting radio frequency cavities. Among these properties is the relatively high transition temperature, the highest of all pure elements. For high purity Niobium this transition temperature has been measured to be 9.25 K. This is well above the boiling point of liquid helium (4.2 K) and so works quite well with standard cryogenic technology. Niobium also has a high thermal conductivity (important in cryogenic environments) and is a very malleable metal (allowing complex cavity geometries to be molded). Niobium also has the advantage of being easily obtainable in pure form.

The layer of niobium oxide (mostly Nb_2O_5) that develops on the surface of all niobium sheets, that which allows the surface to resist corrosion, may also affect the transition temperature by some small fraction of a degree. This niobium oxide layer is typically only 40 Angstroms ($\mathring{A}$) thick. The theory of superconductivity relies on the fact that paired electrons travel freely only in a thin surface layer of the material, the thickness of which is called the London penetration depth. Pure niobium has a penetration depth of roughly 470 $\mathring{A}$. If these paired electrons travel freely only within this thin surface layer then the Meissner effect (flux exclusion) will depend only on the superconducting properties of this surface layer. Since superconductivity is mediated by the electron-phonon interaction, impurities in the niobium lattice affect the mean free path of the electrons. The concentration of impurities within the penetration depth rises as the oxide layer diffuses into the bulk niobium. It could then be possible that the experimental transition temperature may actually be somewhat different than the theoretical value for high purity niobium. The question becomes: In what way is the transition temperature of the niobium sample changed when the oxide layer is absorbed into the penetration depth?

Equipment

The equipment used in this experiment was simple and straightforward. The heart of the experiment is that portion of the equipment shown in Figure 1. The physical understanding governing this piece of equipment is known as the Meissner effect. The Meissner effect is what occurs when a superconducting substance with magnetic flux permeating its volume is cooled through its transition temperature. When the superconducting substance is at a temperature below its transition temperature it will exclude all flux from its volume. The principle relies on the fact that there may be no magnetic flux within the volume of a superconductor in the superconducting state. In the normal conducting state, magnetic flux is allowed to permeate the volume of metal. However, as the metal is cooled below its transition temperature, such that electrons may form pairs and move without friction, internal eddy currents form that oppose the permeating magnetic flux, similar to electric currents that expel magnetic flux according to Lenz's law. These currents bring the internal magnetic flux to zero. All flux has then been excluded from the volume of the metal, with the exception of the thin surface layer in which the flux decays exponentially to a depth roughly equal to the London penetration depth. Figure 1 shows the components used to exploit the Meissner effect. One of the two solenoids is driven by alternating current. This alternating current induces a magnetic field similar to that shown in Figure 2. This magnetic field penetrates the niobium sample by generating surface currents that create a changing magnetic flux in the second solenoid, the pick-up coil. This changing magnetic flux induces

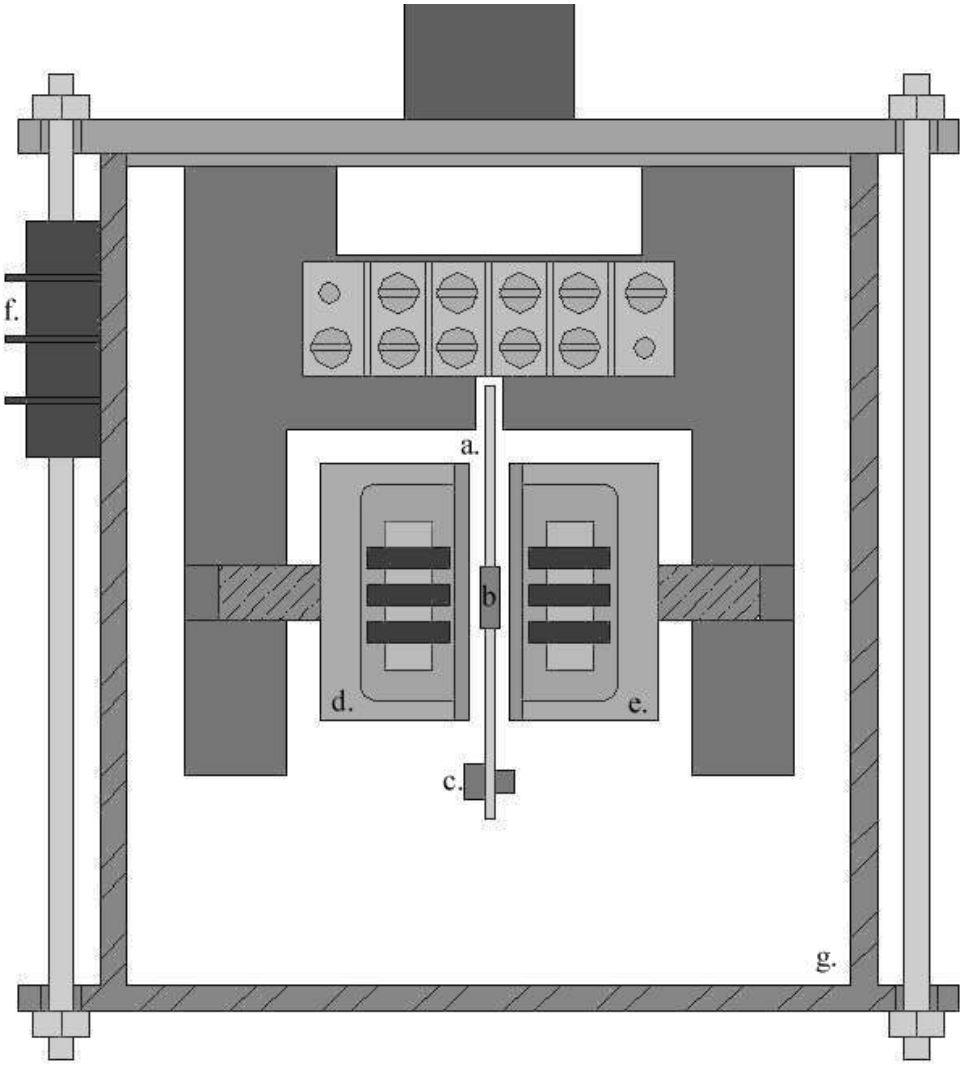

FIGURE 1. The design and construction of the test stand used to secure the niobium sample during testing (wires and leads have been omitted for clarity and the encompassing copper can has been cutaway to reveal enclosed test stand). The long thin element in the center of the Figure is the edge of the niobium sample (a.). Attached to the sample are the two thermometers; (b.) the thin one resting on top and in the center of the sample is the germanium thermometer (a reproducible and accurate thermometer) and (c.) the diode thermometer (for quick convenient temperature readings) is bolted to the hole in the sample just below. To the left and right of the sample are the two coils (solenoids) used to measure the superconducting transition (notice orientation relative to sample): (d.) the execution or driven coil and (e.) the pick-up coil. Just above these are the attachments for all leads and wires operating the system. The black box on the outside of the heating can (f.) provides the electrical connections to drive current through the resistive wire of the heating can (g.). All other elements provide structural support.

an electromotive force in the second solenoid, which causes a current to flow. The voltage across the leads of the second solenoid can then be measured. This voltage gives an indication of how much magnetic flux permeates the niobium sample. As the niobium sample is cooled below its transition temperature the Meissner effect will shield the second solenoid from the magnetic field produced by the driven solenoid (Figure 2). Thus, there should be a significant drop in voltage across the second solenoid in the superconducting state. The voltage will not go to zero, however, since there is some residual flux linkage around the superconducting sample. Figure 1 (and Figure 3) also shows the two thermometers used for measuring temperature. The lower thermometer screwed to the bottom of the sample is a diode thermometer. Above that is a germanium thermometer secured to the middle of the sample. Both thermometers are coated with Apeazon N grease to make good thermal contact to the sample. Also shown in Figure 1 is one component critical to temperature control of the system. This component is a large copper can capable of enclosing the entire coil assembly to provide isothermal conditions. This can is used to slowly heat the sample. The heat is produced by means of 370 feet of highly resistive wire (14.90 Ω/ft.) wound around the can. This wire is connected across 55V to provide roughly 0.55 watts of power. The other component used to control the temperature of the test stand is a large 50 W resistor that rests in the bottom of the cryostat. Used for boiling liquid helium to cool the can with cold helium gas, it is connected across 10V to provide 1 watt of power. The entire coil assembly and heating can were cooled to liquid helium temperatures inside a Cryofab liquid helium cryostat.

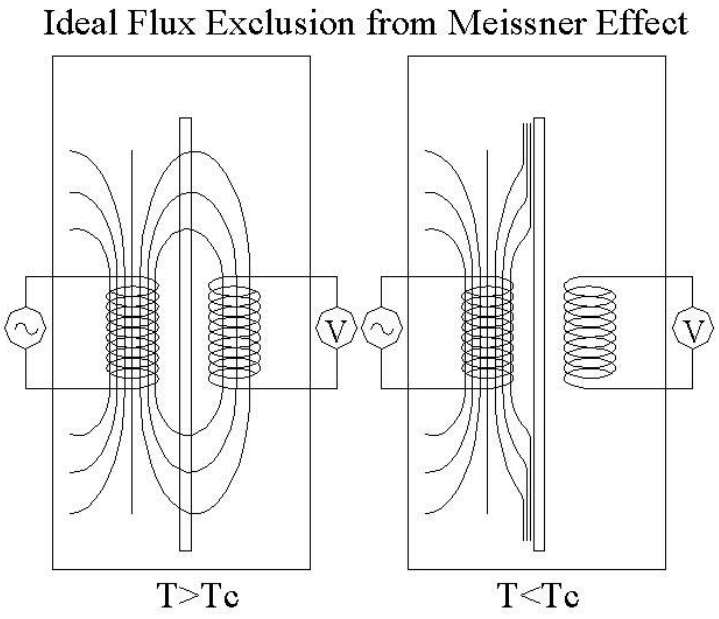

FIGURE 2.

Electronics Setup

The setup of electronics used to monitor this experiment is shown in Figure 3. A signal generator is used to drive an alternating current through one of the solenoids. The signal generator is set to generate a continuous sinusoidal wave at 50 Hz (see calculations section below for choice of frequency). This alternating current runs through the solenoid to generate the ac magnetic field. An amplifier providing enough gain to increase the signal to a few volts first amplifies the induced voltage in the second solenoid. This amplified signal is then sent to a Keithley 197 digital multimeter that measures the voltage. A Lakeshore Cryogenic digital thermometer (model DRC 80) measures the temperature of the diode thermometer attached to the sample and displays the result (the Kelvin temperature scale is used for all measurements). The outer two leads of the germanium thermometer are connected to a thermometer current source operated at 10 μA (microamperes). The two inner leads are connected to a Keithley 195A digital multimeter that measures the voltage drop across the germanium thermometer. The two multimeters and the Lakeshore thermometer are connected to a 7100/66 Apple Power Macintosh computer running LabVIEW. LabVIEW was used to design a program capable of reading data from the GPIB/IEEE 488 interface. Using this interface standard the program reads the amplified voltage from the pick-up solenoid, the voltage drop across the germanium thermometer, and the diode temperature value generated by the Lakeshore thermometer. These data are then saved in one spreadsheet file as concurrent columns. In addition to this equipment an oscilloscope is used to monitor input and output signals from the solenoids.

Collection Method

A typical data run would take between 30-45 minutes. To begin, the outer shell of the cryostat would be filled with liquid nitrogen to pre-cool the inner shell. While this was taking place the niobium sample would be mounted to the test stand. The coils would be adjusted to rest right on top of each surface of the sample (Figure 1). Apeazon N grease is then used to attach each thermometer to the sample; the diode thermometer is bolted to the hole in the sample while the germanium thermometer is placed between the two coils. The heating can is then bolted on and all equipment is checked using the electronic multimeters and thermometers to ensure that a signal is being generated by the sample and to ensure the thermometers are reading properly. Following placement of the 50W resistor, the test stand is lowered into the cryostat. The liquid helium level indicator is then dropped into the cryostat. Once all equipment is setup and working properly the transfer of liquid helium into the cryostat is started. The transfer of liquid helium continues until the level of helium in the cryostat reaches the top of the heating can. After stopping transfer the test stand is raised nearly eight inches so that the liquid helium rests just below the bottom of the heating can. Beginning with the test stand submerged in the liquid helium allows a quick drop to 4.2 K and ensures there will be enough liquid helium in the cryostat to last for several thermal cycles. Once the test stand is raised the heating can is turned on and the voltage source is set to 55V. Once the temperature rises to 8.5 K the LabVIEW program begins to collect voltage and temperature readings. The voltage reading for the germanium thermometer is divided by the 10 μA current value to provide the resistance of the device.

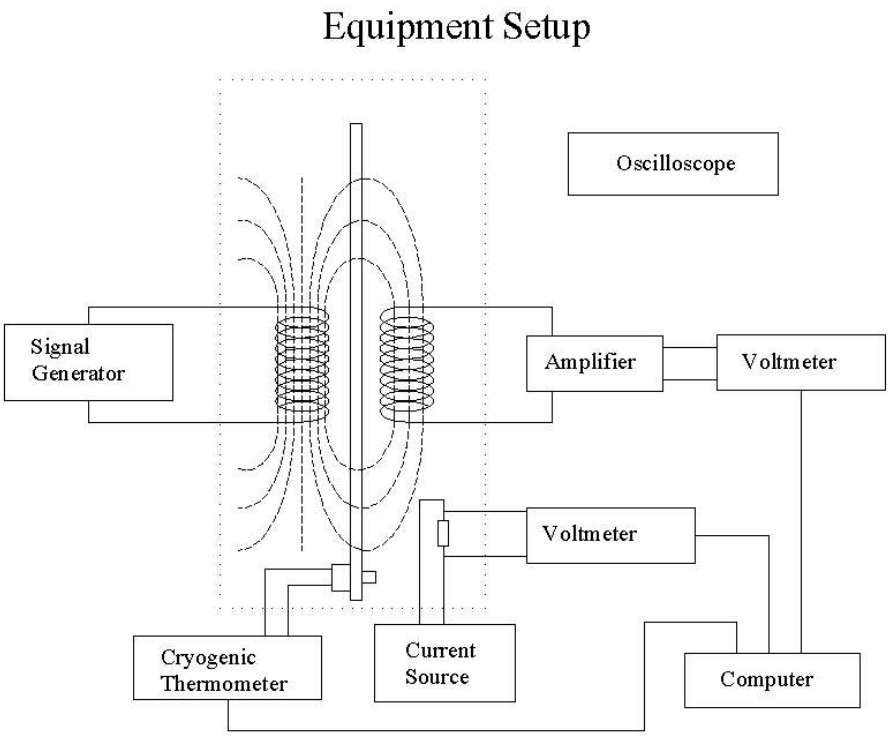

FIGURE 3.

Once 10 K is reached the heating can is turned off, the 50W resistor is turned on, and the voltage source is set to 10V (now operating the resistor). The power generated boils the liquid helium producing gas that cools the heating can and sample. Data collection resumes while the temperature is decreasing and is again stopped at 8.5 K. This can be considered one thermal cycle. This thermal cycling is generally repeated 3 times.

The heating can and 50W resistor were critical to the accuracy and reliability of the experiment. The small hysteresis of the warm-up and cool-down curves were directly related to the rate of change of temperature with time. The greater this rate, the more hysteresis is observed in warm-up and cool-down curves. Therefore, it was necessary to adjust the voltage for each of the two temperature control elements to provide a rather slow temperature transition. Decreasing the rate of change of temperature increased the time for each run significantly but it was much more beneficial having less hysteresis and more accuracy.

Calculations

Skin depth plays an important role in the physics of metals and in the design of this experiment. Alternating current electric fields only penetrate a small distance into the surface of a metal. The field decays exponentially with distance form the surface. Maxwell's equations lead to an expression for the skin depth, the penetrating distance from the surface, of the attenuated fields:

$$\delta = \frac{1}{\sqrt{\pi f \mu_0 \sigma}} \tag{1}$$

For niobium, at 50 Hz $\delta = 2.66$ cm where $\sigma = 7.14 \times 10^6$ $(\Omega\text{m})^{-1}$. Similarly, at 400 Hz $\delta = 0.942$ cm and at 4 kHz $\delta = 0.298$ cm. A typical sample thickness is about 0.159 cm. Although a higher frequency is a better match to the coil impedance, low frequencies are better due to less attenuation from skin depth. Thus, it was necessary to find the best frequency empirically.

The London penetration depth is equally as important to this study as the skin depth. Recall that the penetration depth is the depth at which the exterior magnetic field is allowed to penetrate into the sample in the superconducting state while the skin depth is the depth that an alternating field attenuates to a negligible value. The London theory, extending the usual theory of superconductivity, defines the penetration depth as:

$$\lambda_L = \sqrt{\frac{m_e}{\mu_0 n_s e^2}} \tag{2}$$

where m_e is the mass of an electron, e is the charge of an electron, and n_s is the number of conduction electrons. It must be noted that the penetration depth changes with temperature where at 0 K the value is λ_L and at the transition temperature the value is infinite. However, this temperature dependence can be neglected since we are not interested in measuring the penetration depth. For niobium, the penetration depth is roughly 470 $\mathring{A}$.

Equally important to the understanding of this study is the diffusion of oxygen through niobium. The diffusion of different elements through metals has been well studied. These studies have shown that the diffusion can be accurately estimated from the relationship:

$$d = \sqrt{Dt} \tag{3}$$

where d is the distance from the surface, t is the length of time, and D is the Arrhenius relation given by:

$$D = D_0 e^{-\frac{Q}{kT}} \tag{4}$$

where D_0 is the diffusion coefficient, Q is the activation energy, T is the Kelvin temperature, and k is a constant. For oxygen in niobium between 44-150°C, $D_0 = 2.1 \times 10^{-2}$ cm^2/s, $Q = 29910$ cal/mol, and k is the ideal gas constant $R = 1.98588$ cal/mol-K (all values were taken from reference 5). At a temperature of 140 °C for 48 hours the distance d from the surface that oxygen diffused is approximately 73 $\mathring{A}$. (The values taken from reference 3 indicated that the oxygen diffused 300-500 $\mathring{A}$).

Results

Three niobium samples all made from the same niobium sheet were the primary focus of this study. Each of the three samples were tested several times before heat treatment to calibrate equipment and produce as sharp and as clear a curve as possible. The two niobium samples that underwent heat treatment were tested six times before and six times after being placed in the furnace. Within these six tests were alternating warm-up and cool-down

curves as explained in the Materials and Methods section. The two samples undergoing heat treatment were first etched in a buffered chemical polish (composed of hydrofluoric acid, nitric acid, and phosphoric acid with a volume ratio of 1:1:2, respectively) for 5 minutes to remove surface contaminates before baking. The two samples were then placed in a vacuum furnace (approximately 10^{-6} torr) at 140°C for 48 hours. The results for sample 1 and sample 2 are presented in Figure 4. From both graphs it is evident that the transition temperature decreased by a small fraction of a degree (both curves shifted left after the heat treatment). Also notice that in both curves recorded before heat treatment there is a very subtle bend in the middle of the transition curve. Moreover, near the bottom of the transition curve in both figures there is a much more pronounced bend before the voltage stabilizes (see Figure 4a). The importance of these two characteristics arises when they are compared with the transition curves after the samples underwent heat treatment. Notice that the subtle bend in the middle of the transition curve disappeared and that the distinct bend at the bottom of the transition curve "smoothed-out" to become a more gradual transition to a stabilized voltage. This is especially clear in sample 2 (Figure 4). It is also important to note that the differences in the voltage readings (observe differences between left and right axes) are only due to slight variations of the gain of the amplifier. This and all other data were referenced with the third niobium sample that was used as a control. This third sample did not undergo heat treatment. Graphs of sample 3 transition curve measurements both before and after samples 1 and 2 were baked showed good overlap of warm-up and cool-down curves. Sample 3 also showed the increased voltage signal indicating only that the gain had been adjusted between tests.

Discussion

This study established that baking at 140°C does not raise the transition temperature of the niobium as expected. Instead, just the opposite occurs. The transition temperature decreases by roughly 0.05 K. The study has demonstrated several important effects of baking at 140°C. First, it is important to note that our results do support the results from previous studies regarding the heating of oxidized cavities and the concentration of oxygen in niobium (see reference 3). These studies also showed a slight decrease (from 0.01 K to 0.1 K) of the transition temperature following baking of niobium cavities. There is one problem in the ability of the experiment to detect a drop in the transition temperature of a thin layer of the niobium sample. One would expect that the bulk niobium (with a higher transition temperature) should exclude all magnetic flux so that the outer surface layer (with a lower transition temperature) should not influence the signal received by the pick-up coil.

The most likely explanation for why the results in Figure 4 show a drop in the transition temperature is based on some of the limitations of the experiment. The samples used in the experiment were 1.4 cm in width and 6.4 cm in height. This is anything but an infinite sheet to shield all the magnetic flux produced from the ac driven coil, especially considering the relative size of the coil geometry compared to the size of the samples. This means that a small quantity of the magnetic flux still reaches the passive pick-up coil to induce a voltage. This accounts for the large strength of the signal even after the sample enters the superconducting state. The average voltage decreased by 25% through the transition from

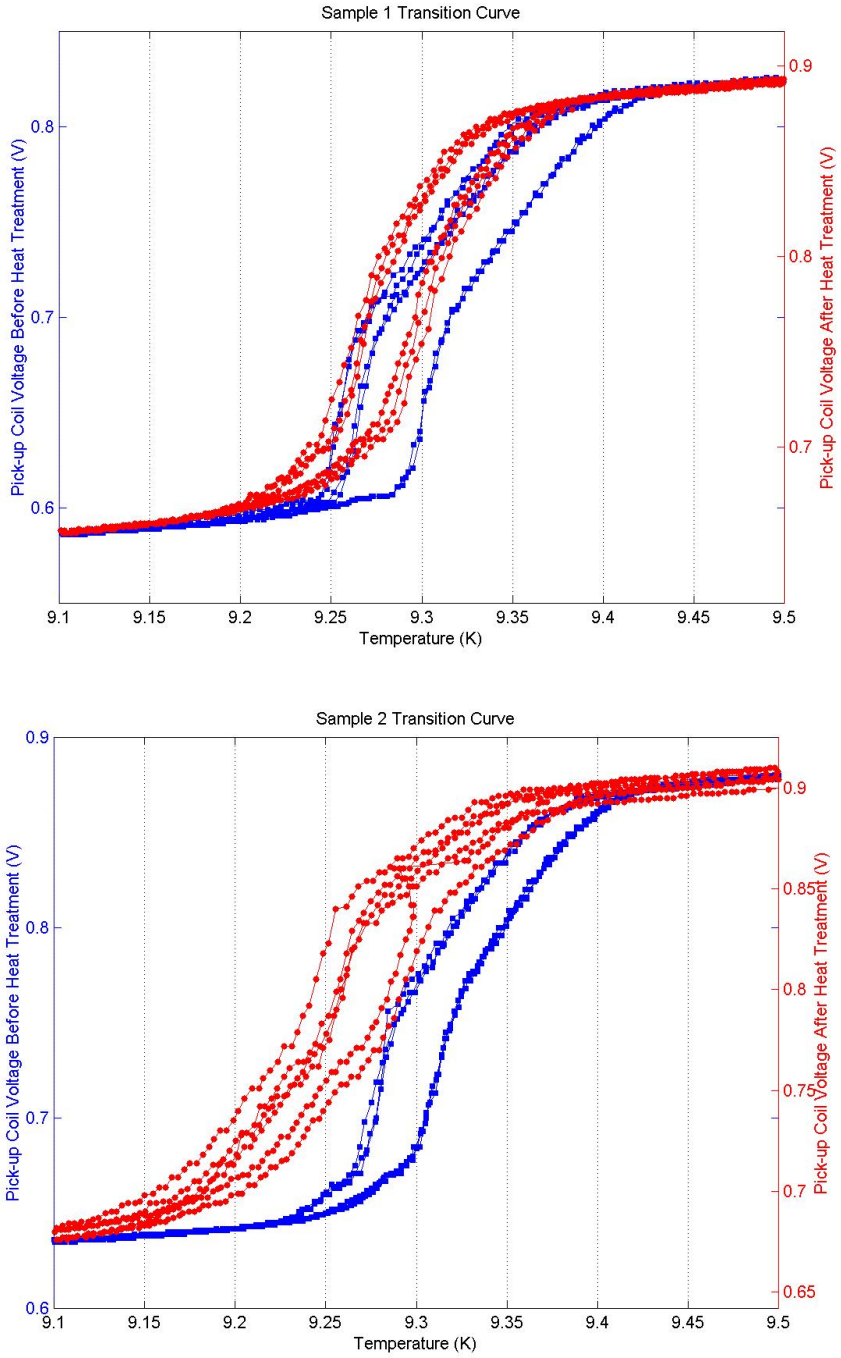

FIGURE 4. Each figure shows the voltage from the passive "pick-up" coil versus the temperature of the sample: in a) sample 1 and b) sample 2. The temperature values were collected from the resistance of a germanium thermometer and converted with a calibration curve from a diode thermometer. The abrupt drop in voltage shows the transition of the niobium sample from the normal to the superconducting state (right to left in the graph). The voltage is a measure of the induced electromotive force in the coil resulting from the amount of magnetic flux permeating the sample. The blue squares are the data collected before heat treatment while the red circles are the data collected after heat treatment.

its value in the normal conducting state [1]. Ultimately, a voltage drop of nearly 100% should be achieved for the most accurate data (although ac solenoids will never reach the full 100% drop as a result of the inertia of the charge carriers). Despite this limitation the voltage drop was significantly large enough to show the full transition and accurately measure the transition temperature of the samples.

The size limitation of the sample also manifests itself in surface layer effects. This is probably the best explanation for the decrease of the transition temperature of the niobium samples. Just as the largest faces of the niobium sample were effected by heat treatment, so too were all other surfaces of the samples including edges and the insides of the holes drilled to hold the thermometers. All of these surfaces were effected by the same rate of diffusion and all contain similar concentrations of oxygen. The oxide layer on the surface of the niobium sample may also be more complex than expected. It turns out that oxygen does not readily diffuse into the bulk niobium metal from the surface oxide layer. There is some sort of oxide "barrier" preventing, or rather limiting, the oxygen's ability to reach the bulk niobium metal and to diffuse according to the predictions. The oxide layer is thus more complicated than the anticipated stoichiometry. Oxygen that does reach the bulk niobium metal is allowed to diffuse according to equations (3) and (4). Despite these problems, it is certain that oxygen did diffuse into the bulk niobium although the exact distance and concentration within the metal is still somewhat uncertain. This surface oxide layer combined with the diffused oxygen concentration in the bulk of the niobium metal has a lower transition temperature as a result of the increased number of impurities per volume (the concentration is what counts here). Due to the rate of diffusion this volume containing impurities is also much larger than before heat treatment. Because this effected volume has a lower transition temperature and increased volume than the sample had before heat treatment, much more flux is allowed to penetrate the sample through this thin surface layer. Therefore, even at the transition temperature of the bulk niobium there will be a slightly higher induced voltage as a result of the increased amount of magnetic flux that now penetrates the contaminated metal where it once was shielded by the transition of bulk niobium. This new magnetic flux will not be shielded until the contaminated niobium enters the superconducting state a few tenths of degree lower than the bulk niobium transition temperature. This could explain the broadening of the shape of the transition curve seen in Figure 4. This broadening occurs near the end of the transition to the superconducting state at a few tenths of a degree lower than where the transition started. It can be interpreted in the following way. The bulk niobium, upon reaching its transition temperature shields the majority of the magnetic flux produced by the driven coil. This begins the voltage drop observed in Figure 4. However, there is still some magnetic flux penetrating the sample through the contaminated volume of niobium near the surface. As the temperature is slowly decreased parts of this contaminated niobium, with higher oxide concentrations, become superconducting thus shielding a little more of the magnetic flux. The difference in concentrations of the oxide impurities through the effected niobium make for different transition temperatures of different volumes of the effected surface niobium. Slowly each of these become superconducting, shielding more and

[1] Improved coil geometries tested between runs in this experiment improved the voltage drop providing a much stronger signal and clearer transition. The average voltage decreased by 75% through the transition with these new coils.

more magnetic flux as the temperature is lowered. Thus there should not be a sudden drop near the end of the transition, but rather a gradual drop to the stabilized voltage. This is seen in Figure 4a and is highly exaggerated in Figure 4b. Ultimately, new coil geometries and improved thermometry systems must be developed to further enhance the accuracy and consistency of these measurements.

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