Surface superconductivity in niobium and niobium-tantalum alloys*

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The critical field for surface superconductivity, H_{c3}, and the upper bulk critical field, H_{c2}, have been measured as a function of temperature and mean free path for Nb and Nb(Ta) alloys in an attempt to study the spatial variations of the superconducting interaction constant $N(0)V$ near a vacuum-metal interface. At temperatures below $T/T_c = 0.85$, the pure-Nb sample shows H_{c3}/H_{c2} values well above 1.695, as predicted by Hu and Korenman for the limit of long electronic mean free path. As the mean free path decreases, there is a regular depression of H_{c3}/H_{c2} toward 1.695. At temperatures above $T/T_c = 0.85$, however, there are striking deviations from the theory which may arise because the interaction constant is slightly depressed at the surface. A model calculation by Hu shows that changes in $N(0)V$ at the surface of 0.7% for pure Nb and 1.6% for Nb-1.0-at.%. Ta can account for the for the experimental results.

INTRODUCTION

The theory of surface superconductivity[1,2] agrees with experiment[3] rather well for temperatures well below the transition temperature T_C. Shortly after Saint James and de Gennes[1] first predicted the existence of surface superconductivity, several experiments[3] confirmed that the ratio of the critical fields (H_{c3}/H_{c2}) was about 1.7, in accord with theory, and the basic idea of surface superconductivity quickly became well established. Indeed, extensions of the original theory to cover the case of materials with long mean free paths also agree with experiment[4,5] at low temperature. At temperatures very close to T_c, however, several investigators[5–7] have observed systematic deviations from the theory which are far outside experimental error. Soon after the discrepancies were found, Hu[8] suggested that the deviations could be explained by a spatial variation of the strength of the interaction parameter, $N(0)V$,[9] and he performed model calculations which showed that the data could be fit rather well if $N(0)V$ changes by as little as a few percent for a distance comparable to the coherence distance at $T=0$, $\xi(0)$, near the surface. The purpose of this work is to test the Hu model for a wide range of normal-state mean free paths l. If the Hu explanation is correct then the temperature dependence of H_{c2} and H_{c3} can be used as a tool to study the spatial dependence of $N(0)V$ near a vacuum-metal interface.

EXPERIMENTAL

Sample preparation

Dissolved gases strongly affect the superconducting properties of Nb so an important aspect of this research is the removal of these gases and the preparation of clean surfaces. Some time ago De Sorbo[10] showed that dissolved oxygen can depress T_c of Nb by 0.93 K per at.% oxygen, and it can lead to rather broad transitions. Fortunately most of the dissolved gases can be removed from Nb and clean surfaces can be prepared by outgassing at temperatures near the melting point in a high vacuum. Hence the general approach adopted here is to heat the sample by electron bombardment to a temperature of about 2000 °C for several hours in a vacuum of 10^{-9} Torr and then to cool the sample and seal it in a Pyrex tube without exposure to air. Most of the samples were prepared in this way but some were subsequently anodized.

The Nb metal used in this work was obtained from the Du Pont Corp. (Lot No. CDH-43-9). To prepare the samples, pure Nb was arc melted and then electron-beam melted into a button about 3.75 cm in diameter. This button was then cut into pieces and arc melted with appropriate quantities of Ta to form the alloys. Each of these buttons was then swaged and drawn into 0.075-cm-diam wires, electropolished in a 2% sulfuric-acid–methanol mixture at −70 °C for 5 min, and cut into 3.75-cm-long pieces. Near one end of this wire, a 0.63-cm segment was rolled into a ribbon approximately 0.013 cm thick and 0.075 cm wide. The purpose of this was to provide a region where the sample could be melted easily to separate the desired portion of the sample from the spot-welded section after outgassing. If this section were not thin then the surface tension is larger than the weight of the sample and the wire melts into a ball rather than dropping into the Pyrex capillary, shown in Fig. 1.

To outgas the sample, the flattened end of the wire was spot welded to a tungsten electrode and mounted in a high-vacuum electron-bombardment apparatus shown in Fig. 1. Normally the sample was heated to about 2000 °C in a vacuum of about 2×10^{-9} Torr. At this temperature and pressure, the absorption and evaporation rates give a sample

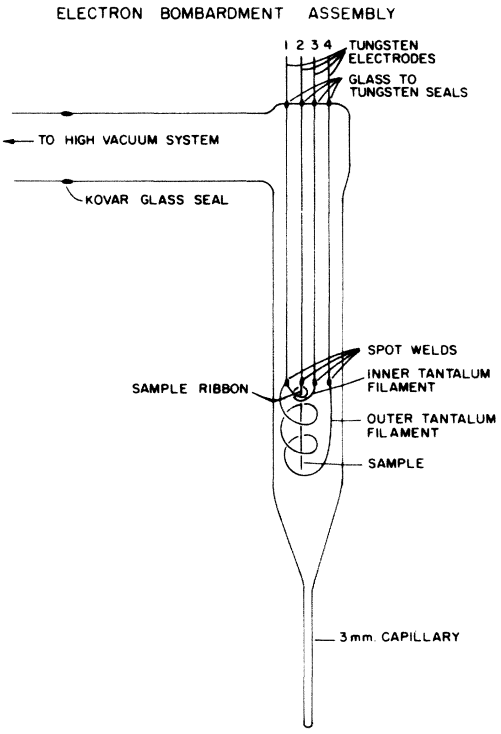

FIG. 1. Electron-bombardment apparatus for outgassing the samples and cleaning the surface. After sample preparation, the thin-ribbon section near the top was melted and the sample dropped into the capillary.

with concentrations of a few ppm N and O.[11] After 24 h at 2000 °C the power was abruptly stopped and the sample cooled to less than 500 °C in less than 2 sec. After the sample had cooled 2 to 3 h in the high vacuum, a small filament wrapped around the ribbon section of the wire was used to melt the wire and separate the sample from the electrode. The sample then dropped into a capillary tube. The vacuum pump was then shut off and the system was filled with 99.999%-pure-He gas to a pressure of about 600 Torr. The sample was then sealed inside the glass capillary with a torch.

Results of the analyses of the samples made after the superconducting measurements are shown in Table I. Ta and W were determined by neutron activation to better than 10%. N, O, and H were determined to about 10% by mass fusion. Other trace impurities were determined by mass spectroscopy. The only element for which a good analysis was not made was carbon, but previous work[12] indicates that the carbon content should be less than 100 at. ppm.

Cryostat

The apparatus used in this work was a conventional heat-leak chamber suitable for use between 1 and 20 K. To ensure thermal equilibrium, the sample, the pickup coils, and the thermometers were mounted in a brass yoke which was then mounted inside a sealed brass can. This whole interior assembly was then exposed to He^4 gas at a pressure of 0.2 Torr to aid the thermal equilibrium. This inner can was then isolated from the liquid-He^4 bath by an evacuated chamber in the usual way. Temperature stability of 0.0001 K was routinely maintained for period of 5 min and stability of 0.001 K was maintained for several hours as needed. Values of the temperature were determined by the same germanium thermometer (GR 99) used in earlier work.[12]

The primary dc magnetic fields were generated by a liquid-nitrogen-cooled solenoid which was calibrated by proton resonance in glycerine to give 152.45 ± 0.02 Oe/A for 6 different fields between 1700 and 3300 Oe. The power supply for the magnet was a Spectromagnetic current-regulated supply which was stable to one part in 10^5 for periods of several hours. The earth's magnetic field was compensated to approximately 0.01 Oe by Helmholtz coils. Mutual-inductance coils for the ac susceptibility measurements were wound astatically on nylon forms and oriented so that the ac exciting field and the steady dc field of the liquid-nitrogen-cooled solenoid were parallel to the axis of the cylindrical sample.

RESULTS AND DISCUSSION

Permeability curves

The general shapes of the magnetic field dependence of the real and imaginary parts of the permeability (μ' and μ''), as shown on Fig. 2, are similar to the results reported earlier.[4,5] H_{c1} was defined as the field where μ' is half-way up the first peak, and H_{c2} was taken to be the high-field shoulder of the second peak. These identifications agree well with magnetization data[12] and are reproducible from sample to sample. Above H_{c2}, μ' monotonically approaches the normal-

TABLE I. Results of the chemical analyses for several samples (at. ppm).

Sample	Ta	O	N	H	Fe	W
H-7, Nb	43	13	<1	<1	5	
H-9, Nb[a]	110					48
H-26, Nb[a]						
H-15, Nb-1 000-ppm Ta	730	<1	<1	<1	10	44
H-19, Nb-1 000-ppm Ta[a]	1 150					
H-13, Nb-5 000-ppm Ta[a]	5 590					
H-21, Nb-5 000-ppm Ta	6 320	5	<1	<1	5	48
H-10, Nb-10 000-ppm Ta	10 300	60	<1	<1	1	48
H-11, Nb-10 000-ppm Ta[a]	10 600					
H-23, Nb-20 000-ppm Ta[a]	22 100					
H-27, Nb-20 000-ppm Ta	25 100	6	<1	<1	10	43

[a]Samples used for ac susceptibility measurements.

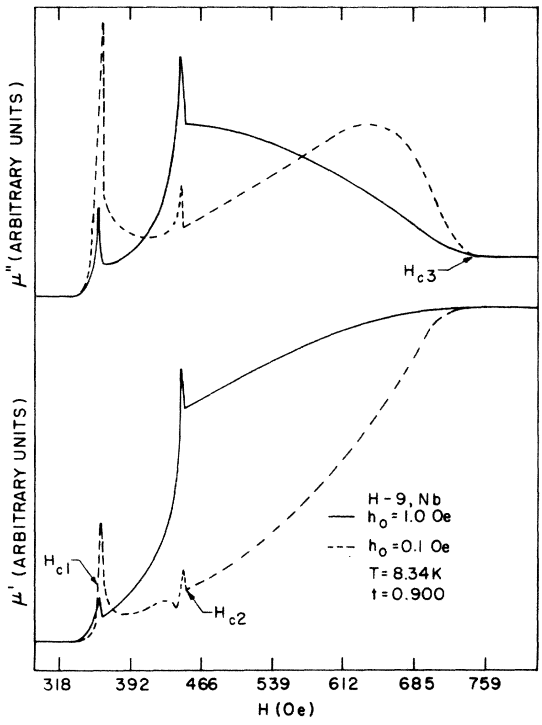

FIG. 2. Permeability curves for pure Nb at two different measuring fields.

state value, whereas μ'' either goes through a maximum or monotonically approaches the normal-state value depending on the value of the ac measuring field. H_{c3} is somewhat more difficult to define than H_{c1} and H_{c2} because there is considerable rounding.[13] The critical-current model for the surface sheath discussed by Rollins and Silcox[14] suggests that μ'' curves give a more sensitive measurement of H_{c3} and we find this to be the case for these samples. Hence H_{c3} was taken as the intersection of straight-line portions of the μ'' curve above and below H_{c3}.

Several factors which can alter the detailed shape of the μ' and μ'' curve were studied in some detail. As shown in Fig. 2, the magnitude of the peaks at H_{c1} and H_{c2} change substantially as the magnitude of the ac measuring field, h_0, is varied, but the values of H_{c2} and H_{c3} do not change. At fields above H_{c2} the peak in μ'' shifts to lower fields with increasing h_0, as predicted from the critical-current model.[14] Values of the critical shielding currents J_c shown on Fig. 3 are about 0.2 A/cm at H_{c2}. These values are somewhat smaller than earlier measurements with Pb-In alloys[14] but larger than values for Ti-Nb alloys.[15] No adequate theory yet exists to explain the small magnitude of J_c.[16]

Two other factors which might influence the phase boundaries were sample alignment and hysteresis on the μ'-vs-H plots. Small errors in aligning the sample axis with the applied field[14] can make substantial changes in the μ' and μ'' curves, but the values of H_{c1}, H_{c2}, and H_{c3} are not changed by more than 1% as long as the alignment is within 1°. Misalignments up to 3° were studied.

Between H_{c2} and H_{c3}, the magnitudes of the μ' and μ'' for increasing values of the dc magnetic field are essentially the same as those for decreasing H so that there is little hysteresis in the μ'- or μ''-vs-H plots in this region. Between H_{c1} and H_{c2}, however, the field-decreasing μ' plots lie much closer to the normal-state values than the field-increasing μ' plots and the magnitude of this effect varies from sample to sample. This effect was too irreproducible to warrant a thorough study. The values of H_{c1} and H_{c2}, however, do not change even though the hysteresis changes. Detailed discussions of these effects are available elsewhere.[13]

For pure Nb and the 5000-ppm-Ta sample the superconducting-to-normal transitions are 0.004 and 0.006 K wide, respectively, so the samples are rather homogeneous. In addition, the shape of the μ'-vs-H and μ''-vs-H curves remain unchanged right up to a reduced temperature of $t = 0.996$, providing h_0 is sufficiently small. This is similar to results reported earlier[4] for a different pure-Nb sample. For the 10 000-ppm alloy, however, the zero-magnetic-field transitions are nearly 0.040 K wide and there is some broadening of the μ'-vs-H curves for all temperatures above $t \simeq 0.96$. This effect then limits the temperature range over which measurements are meaningful for this sample to temperatures below $t = 0.96$.

Vortex state characteristics

For all the samples reported here, the vortex-state parameters agree well with the Ginsburg–

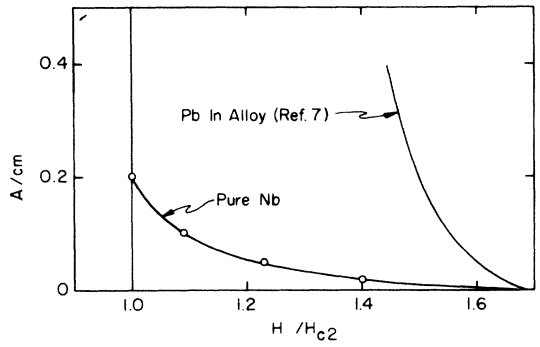

FIG. 3. Critical currents deduced from the maximum in the μ'' vs H curve.

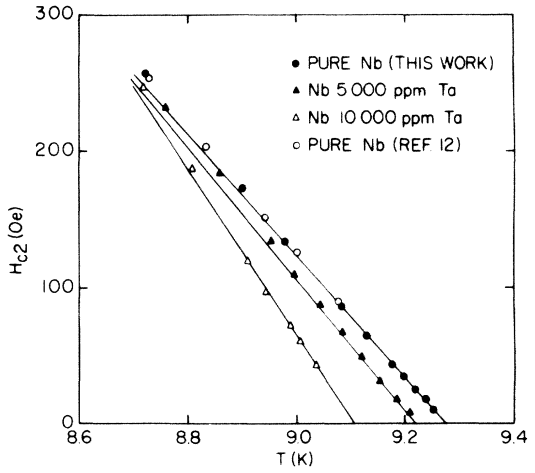

FIG. 4. Temperature dependence of H_{c2} near T_c.

Landau theory near T_c.[17] As shown in Fig. 4, H_{c2} has a linear temperature dependence with a slope which increases with increasing Ta content. The increase in slope is expected, of course, because the Ginsburg–Landau parameter κ increases. To determine the numerical value of κ for each sample, the measured normal-state resistivity ρ_n was used in conjunction with the equation $\kappa = k_0 + (7.53\times10^3)\rho_n\gamma^{1/2}$, where k_0 is a constant equal to 0.76,[12] ρ_n is measured in $\mu\Omega$ cm, and γ is the specific-heat coefficient measured in erg/cm^3 K.[2] In addition, one can calculate the London penetration depth at $T=0$, $\lambda_L(0)$, from the relation[18]

$$\lambda_L(0)=\left[\frac{\pi\sqrt{2}}{\varphi_0\kappa}\frac{dH_c}{dt}\right]^{-1/2},$$

where φ_0 is the flux quantum equal to 2.07×10^{-7} G cm^2. One can also calculate the coherence distances ξ_0 from

$$\xi_0\cong 0.96\,\lambda_L(0)/\kappa$$

if we assume that all these samples are essentially in the clean limit. Values of each of these parameters are given in Table II for four different values of x, the Ta concentration.

Surface superconductivity

For temperatures below a reduced temperature, $t=T/T_c$, of 0.7 the data agree rather well with the original theories,[1,2] as shown on Fig. 5. The ratio of H_{c3}/H_{c2} for pure Nb lies between the pure-limit Hu and Korenman (HK) theory shown by the dotted line and the dirty-limit Saint James and de Gennes (SJdG) theory shown by the dashed line. Indeed, as the sample is made dirtier by adding Ta, H_{c3}/H_{c2} approaches the dirty limit.

For temperatures near T_c, however, the data deviate sharply from the theory[1,2] and approach 1.0 rather than 1.695. This is a very large effect which can clearly be seen from the μ''-vs-H curves of Fig. 6. Here, the data are plotted in terms of the reduced field H/H_{c2} to emphasize the large decrease in H_{c3}/H_{c2} as the temperature approaches T_c. There are some small changes in the shape of these μ'' curves which arise because the ratio of the measuring field h_0 to H_{c2} changes, but basically the curves have the same shape and there is no difficulty identifying either H_{c2} or H_{c3}. H_{c3}/H_{c2} systematically falls well below 1.695 and approaches 1.0 as T goes to T_c.

A number of variables have been systematically changed to search for the origin of this effect. The coherence distance has been lowered by adding Ta and the deviations from the theory, as shown on Fig. 5, occur at successively lower temperatures. Qualitatively, however, the behavior is similar to pure Nb. A study was also made of a pure-Nb sample which had been anodized after the standard outgassing and the results are almost identical to the vacuum-cleaned surface, as shown by the diamonds of Fig. 5. In an earlier work a study also was made of samples

TABLE II. Sample characteristics for the Nb(Ta) alloys.

x (ppm Ta)	100	1 000	5 000	10 000
T_c (K)	9.273	9.259	9.226	9.079
	±0.002	±0.002	±0.003	±0.020
ρ ($\mu\Omega$ cm)	0.009 06	0.0525	0.0967	0.38
κ	0.78	0.88	0.98	1.64
$\lambda_L(0)$ (Å)	3.14	334	353	456
$\xi(0)$ (Å)	387	364	343	268
l (Å)	120 000	21 000	11 000	2900
$D/\xi(0)$	~2.3	~2.3	~2.3	~2.3
V_1/V_1	0.0076	0.0080	0.0096	0.016
Z'	0.039	0.040	0.049	0.078
H_{c3}/H_{c2} ($T=0$)	1.888	1.886	1.878	1.846
$\xi(0)/b$	0.019	0.022	0.029	0.044
$\xi(0)/\kappa b$	0.025	0.025	0.029	0.027

exposed to air and again the results were similar to the Ta alloys. Every sample we have measured behaves much like the samples shown in Fig. 5. These deviations from the theory are very large and are well outside experimental uncertainty or errors in defining H_{c2} or H_{c3}.

One very reasonable model which can explain these results has been presented by Hu.[8] He has suggested that the rapid depression of H_{c3} near T_c arises because the superconducting interaction constant $N(0)V$ is slightly depressed near the surface and he has worked out the temperature dependence of H_{c3}/H_{c2} for the case where $N(0)V$ is depressed by a constant amount, $N(0)V_1$, for a distance D from the surface. The two important dimensionless parameters in the model then are $D/\xi(0)$, which measures the range of the perturbed interaction, and $N(0)V_1/N(0)V$, which measures the strength of the perturbation. To fit the results numerically one divides the data into three temperature regions depending on the relative size of the temperature-dependent coherence distance $\xi(T)$ and D. At low temperatures (region A)[8] the thickness of the sheath is less than D and H_{c3}/H_{c2} is depressed below the HK theory[2] by a constant amount given by

$$\delta h = \frac{3.85\, V_1/V}{N(0)V},$$

where

$$\delta h \equiv H_{c3}/H_{c2}\big|_{\mathrm{HK}} - H_{c3}/H_{c2}\big|_{\mathrm{data}}.$$

At intermediate temperatures (region B),[8] for which $\xi(t)$ is greater than D but not much greater than D, Hu predicts

$$\delta h = z'\,\epsilon^{-1/2},$$

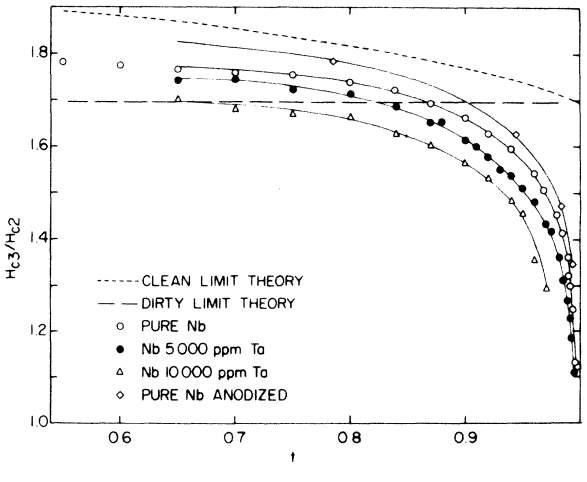

FIG. 5. Temperature dependence of H_{c3}/H_{c2} for a variety of samples. The clean-limit curve is from the HK theory and the dirty-limit curve is from the SJdG theory.

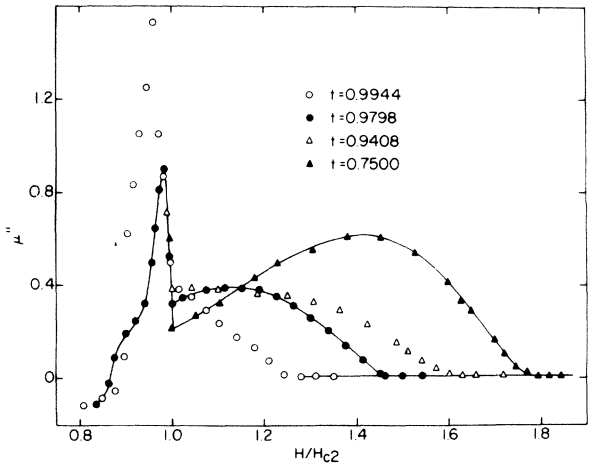

FIG. 6. Magnetic field dependence of μ'' at several different temperatures.

where $\epsilon^{-1/2} = (1-t)^{-1/2}$ is the divergent factor for $\xi(t)$ and

$$Z' = \frac{2.007}{N(0)V}\left(\frac{-V_1}{V}\right)\frac{D}{\xi(0)}$$

is a constant characteristic of the material. In the limit where $\xi(T) \gg D$ (region C), δh does not approach infinity but approaches 0.695 as the broad sheath sees an average interaction constant which approaches the bulk value.

To see how well the model fits the data, we have plotted δh for several samples vs $\epsilon^{-1/2}$ on Fig. 7. For $t > 0.8$ all the samples show approximately a straight line with somewhat different slopes, and all the samples approach $\delta h = 0.695$ as expected. All of the samples change behavior rather dramatically at $t \approx 0.8$ or $\epsilon^{-1/2} = 2.3$, and we take this to be the boundary between region A and region B. Within the model this is the temperature for which the sheath thickness is equal to D; so we would predict that $D \approx 2.3\,\xi(0)$ for all of these samples. This means that the range of the perturbed interactions scales with the $T = 0$ value of the coherence distance. From the values of the slope Z' one can also calculate that the magnitude of the perturbation varies from 0.76% for pure Nb to about 1.6% for the 10 000-ppm-Ta alloy. Values of all these parameters are summarized in Table II. This is a very small perturbation. Apparently the rather large changes in the electron-phonon interaction which might take place at the surface of a metal are averaged out in their effect on the superconducting order parameter so that the average effect is only about 1% over a rather substantial distance of about $2.3\xi(0)$.

Another way to parametrize the data would be to arbitrarily adjust the slope of the wave function[17]

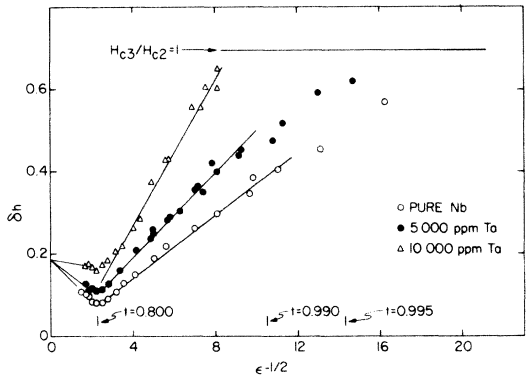

FIG. 7. Graphical fit of the data to the Hu model. δh is the deviation of the data from HK and $\epsilon = 1 - t$.

at the vacuum-metal interface to give the measured value of H_{c3}/H_{c2}. There is no full theory to convert H_{c3}/H_{c2} measurements into an effective slope

$$b = \frac{1}{\Psi}\frac{\partial \Psi}{\partial x},$$

but with the calculations of Fink and Joiner[19] as a guide one can estimate the ratio of $\xi(0)/b$ to range from 1.9% for pure Nb to 4.4% for the 10 000-ppm-Ta sample. It is interesting to note that $\xi(0)/b\kappa$ is very nearly a constant, but at present we do not understand this observation. A very small change in the slope of the order parameter can make drastic changes in the magnetic field range of sheath superconductivity near T_c. Hence the condition of the surface which governs the boundary condition on the superconducting wave function must be carefully controlled. Small amounts of metallic NbO[20] on the surface, for example, could make important changes in the slope of the order parameter.

Anodization experiments

Recent experiments at Karlsruhe and Argonne[21] indicate that anodization can be an effective way to produce a clean metal-insulator interface between the Nb metal and the Nb_2O_5 insulator. When Nb is exposed to air a variety of different oxides can form and at least one of these oxides, NbO, is metallic and a superconductor with a transition temperature of about 1.38 K.[20] To produce a surface for which there is a simple boundary condition on the wave function it is important to remove the NbO normal-metal layer and convert it to Nb_2O_5 insulator. Anodization may provide a way to do this. Nb_2O_5 has a dielectric constant close to 1 so the Saint James–de Gennes boundary conditions should apply for a Nb-Nb_2O_5 interface.

To prepare the sample a niobium wire was outgassed as described earlier and anodized for 20 min at 20 V in a 0.2-N H_2SO_4 electrolyte. This presumably gives a 400-Å layer of Nb_2O_5 on the surface of the sample. H_{c3}/H_{c2} data shown by the solid triangles of Fig. 5 are very close to the unanodized pure-Nb sample. There is a very slight shift toward the clean limit, so this would seem to indicate that the anodized sample has a cleaner metal-insulator surface than any of the other samples.

End effects

A small, but important, experimental detail remains concerning the reproducibility of the susceptibility data from sample to sample. Finnemore *et al.*[12] found that the shape of the μ' and μ'' curves for pure Nb varied a great deal from sample to sample, but this was not the case for samples reported here. In the earlier measurements[12] the samples were about as long as the mutual-inductance coil, whereas in this work the samples were longer than the coils, so there was a good chance that sample-end effects were the cause of the irreproducibility. A series of measurements with the mutual-inductance coils placed at different positions along the sample revealed that a variety of different shaped μ' and μ'' curves similar to those reported earlier could be reproduced by moving the coil near the end of the sample. Hence the lack of reproducibility reported earlier probably arises from end effects.

Frequency dependence of H_{c3}/H_{c2}

In all the measurements discussed so far, the ac field was set at 31.9 Hz so the measurements might reflect the dynamic response of vortices to time-varying fields. In a way, 31.9 Hz could be considered to be essentially dc because 31.9 Hz is slow compared to the time scale of most superconducting phenomena. Vortices might have important time-delay phenomena, however; so a brief study was made of the frequency dependence of the H_{c3}/H_{c2} results.

The most prominant effect of frequency changes arises from variations in the normal-state skin depth. For the pure-Nb sample the normal-state skin depth at 31.9 Hz is about 0.9 mm and the radius of the specimen is 0.38 mm, so μ'' changes radically as the frequency changes from 11 to 11 000 Hz. The change in μ'' from the superconducting to the normal state was approximately proportional to the square of the frequency, but a detailed study of this effect was not undertaken. The μ' curves retain a shape similar to Fig. 2 and these curves were used for the determination of the critical fields.

The most important result of the frequency studies was that H_{c1} and H_{c2} are independent of frequency f as expected, but H_{c3} increases a small but

measurable amount. The magnitude of the increase is about 5% of H_{c2} as f increases from 11 to 11 000 Hz and it is essentially independent of temperature. Hence the ratio of H_{c3}/H_{c2} can be written as the sum of a temperature-dependent term and a frequency-dependent term of the form

$$\frac{H_{c3}}{H_{c2}}(T,f)=\frac{H_{c3}}{H_{c2}}(T,f=1)+0.015\log_{10}f\ .$$

At any given frequency the curves are similar to Fig. 5. The effect of changing the frequency is qualitatively similar to the effect of changing mean free path.

SUMMARY

The striking deviations of the ratio of H_{c3}/H_{c2} from the theory which have been reported earlier have been confirmed for a wide variety of samples, sample surface conditions and normal-state mean free paths. It is a large effect well outside experimental uncertainty.

A detailed analysis of the temperature dependence of H_{c3}/H_{c2} near T_c shows that deviations of the data from the theory diverge as $(1-t)^{1/2}$. If the results are fit to a model proposed by Hu, then the data indicate that the effective superconducting interaction constant is depressed by about 1% in a region of about 2 coherence distances at the surface.

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