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Resistive Transition and Current Density Characteristics in Superconducting Niobium Containing Dissolved Gases*

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Oxygen and nitrogen as interstitial solutes in niobium cause the metal in transverse field to exhibit anomalous resistance minima or critical current maxima (peak effect). The anomaly appears at H_{c2}, the upper critical field of these Type II superconductors. The resistance in the mixed state is decreased by exceeding the solubility limit, by cold working and by strain aging at 170°C, masking out the anomaly. Rapidly quenching from the solution temperature decreases the anomaly. The results suggest that the anomaly is strongest at some intermediate stage of the process of segregation and precipitation at dislocations. Resistance in the mixed state is increased by introducing more solute, by quenching, and by etching. Structural changes brought about by cold working, strain aging, and rapid quenching responsible for large changes in $J_c(H)$ or $R(H)$ in the mixed state also cause changes in the region $H_{c2}<H<H_{c3}$. In this latter region, field orientation effects and observed H_{c3}/H_{c2} ratios are roughly consistent with the concept of a superconducting surface sheath as recently proposed by Saint-James and de Gennes. Pure niobium, however, tends to exhibit consistently higher ratios.

I. INTRODUCTION

SUPERCONDUCTING transition metals in Group V of the periodic table have been noted for their anomalous behavior which is usually attributed to the presence of chemical and/or structural impurities. An important metal of this group is niobium, which serves as a base metal in the fabrication of many high-field, high-current-carrying superconductors. The influence of substitutional[1] and interstitial[2] solutes on some superconducting properties of noibium has been recently summarized. Other investigations have also appeared, revealing the importance of small amounts of interstitial impurities on the substructures of the metal (e.g., see Ref. 3).

Unusual superconducting behavior occurring in niobium has been reported in both the resistance-field[4] and critical current-field characteristics.[5] Recently, some striking resistance decreases following an initial rise were observed[6] during the superconducting transition of the metal: (a) when the current I through the wire, and temperature T were kept constant and a transverse magnetic field was increased continuously; or (b) when the current and field were held constant and T varied. The field at which the resistance minimum takes place was found to be independent of J, occurring at a field comparable to the upper critical field, H_{c2} of a Type II superconductor.[7,8] It is pointed out in this report that this anomalous behavior is readily observed in niobium containing small amounts of interstitial solutes such as oxygen or nitrogen but is not observed in outgassed niobium. The results are compared with the magnetic behavior of the solutions which have already been described[2] as Type II superconductors. The influence of solute concentration, field orientation, cold working, strain aging, quenching, and etching on the resistance-field transition and on the current

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2 W. DeSorbo, Phys. Rev. **132**, 107 (1963).
3 J. O. Stiegler, C. K. H. Dubose, R. E. Reed, Sr., and C. J. McHargue, Acta. Met. **11**, 851 (1963).
4 T. G. Berlincourt, Phys. Rev. **114**, 969 (1959).
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6 S. H. Autler, E. S. Rosenblum, and K. H. Gooen, Phys. Rev. Letters **9**, 489 (1962).
7 A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **32**, 1442 (1959). [English transl. Soviet Phys.—JETP **5**, 1174 (1957)].
8 B. B. Goodman, IBM J. Res. Develop. **6**, 63 (1962).

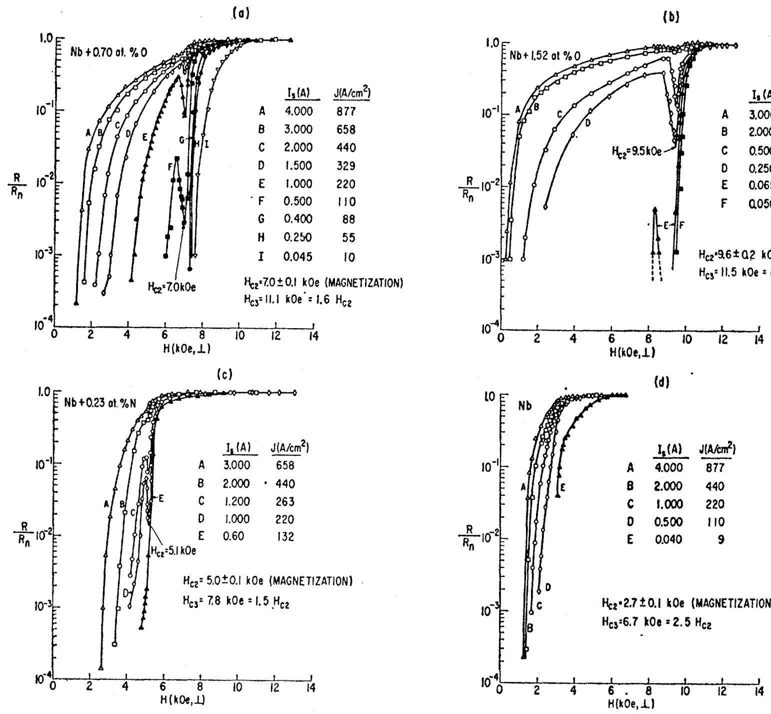


FIG. 1. The resistive characteristics R/R_n as a function of current density and applied transverse field at 4.2°K for wire (0.030-in. diam) specimens of (a) Nb+0.70 at.%O ($T_c=8.7_8$°K); (b) Nb+1.52 at.%O ($T_c=8.0_4$°K); (c) Nb+0.23 at.% N ($T_c=9.20$°K); and Nb ($T_c=9.4_6$°K). H_{c3} values are evaluated at $J\approx 10$ A/cm².

density-field characteristics both in the mixed state below H_{c2} and in the region $H_{c2}\leqslant H\leqslant H_{c3}$ are summarized. The dependence of H_{c3}—the field at which the specimen is completely normal—on these factors is cited.

II. EXPERIMENTAL

The niobium wire specimens (0.030-in. diam) were made from an electron-beam melted stock obtained from the Stauffer-Temescal Company, Richmond, California, hereafter referred to as Nb(S-T) (see Ref. 2). Rods, about 0.250-in. diam were machined from the ingot then swaged and drawn to wire form. The resistance ratio, $R_{298°\mathrm{K}}/R_{10°\mathrm{K}}$, of the wire "as received" was about 110. The quantitative addition of the interstitial solute was carried out by a procedure developed earlier by Powers and Doyle[9]. The interstitial solute was introduced at temperatures between 1000–1100°C. The specimen was then homogenized by heating at about 1200–1300°C for approximately 1 h. Prior to the introduction of the gas, the specimen had been annealed and outgassed at about 1800–2000°C for several hours at a residual pressure less than 1×10^{-7} mm Hg. After this treatment and prior to the introduction of the interstitial, the resistance ratio of the wire was about 500. An analysis of a similarly prepared specimen reported by Seybolt[10] gave oxygen content 6±3 ppm and nitrogen content 5±3 ppm.

The resistance transition as a function of field at constant current density was measured at 4.2°K potentiometrically with a noise level less than 0.1 μV. Referred to in terms of R/R_n, where R is the resistance in the transition and R_n, the normal resistance, the noise level is less than 1×10^{-3} except for data obtained with low current densities ($J<125$ A/cm²) for outgassed niobium. The critical current of the wire specimen in a given field was also measured potentiometrically and the value taken was that which produced approximately 0.1 μV across the potential leads. The fields were produced by a small niobium wire (0.004-in. diam) wound iron-core magnet (0.040-in. slot) designed and built by H. R. Hart, Jr., following an original design due to Autler.[11] Field direction was in all cases transverse to the wire and to current flow. Field orientation for ribbon samples, either perpendicular ($H\perp$w.s.) or parallel ($H\|$w.s.) to the wide surface were obtained by mounting the ribbon in a form permanently fixed between the pole pieces.

The magnetic induction measurements were carried out by a technique used earlier by Bean.[12] A typical

[9] R. W. Powers and Margaret V. Doyle, J. Appl. Phys. **28**, 255 (1957); J. Metals **9**, 1285 (1957).

[10] A. U. Seybolt (private communication).

[11] S. H. Autler, D. B. Montgomery, and G. Ajootian, Quarterly Progress Report on Solid State Research, Lincoln Laboratory, MIT, July 1960, p. 63 (unpublished).

[12] C. P. Bean, Marget V. Doyle, and A. G. Pincus, Phys. Rev. Letters **9**, 93 (1962).

sample prepared for these measurements consisted of 7–10 wire segments, approximately 1.2 cm long, bundled together into a cylindrical form in a paper "straw." The ends of each wire were etched (50% HF, 50% HNO_3) to remove any strains. The sample cylinder was immersed in liquid helium at zero field. Magnetization measurements were made at 4.2°K by flipping it in and out of a copper coil (about 2000 turns) coaxial with an external steady field. The coil was connected to a flux meter whose deflection was proportional to the magnetization of the specimen. The magnetic field measurements were accurate to ±10 Oe; while $-4\pi M$ values were accurate to ±5 Oe.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Influence of Oxygen and Nitrogen in Niobium

1. Resistive Transition at Constant Current Density

The resistive transition R/R_n as a function of transverse field H and current density J at 4.2°K for four wire specimens of niobium containing (a) 0.70 at.% oxygen, (b) 1.52 at.% oxygen, (c) 0.23 at.% nitrogen, and (d) niobium outgassed and annealed is shown in Fig. 1. The resistance decrease in the transition, after an initial rise, is apparent for each of the interstitial solid solutions of niobium containing oxygen or nitrogen at current densities below a maximum value $J_{\max}$ and above a minimum value $J_{\min}$. The drop in resistance is most pronounced at current densities near $J_{\min}$. Increasing the interstitial concentration in the homogeneous solid solution tends to decrease both $J_{\min}$ and $J_{\max}$. For example, for specimen Nb+0.70 at.% oxygen, $J_{\max}\sim 1000$ A/cm² and $J_{\min}\sim 90$ A/cm²; while for specimen Nb+1.52 at.% oxygen, $J_{\max}\sim 800$ A/cm² and $J_{\min}\sim 12$ A/cm². For a given specimen, the field corresponding to the maximum decrease in R/R_n, after an initial rise, appears to be almost independent of J and coincides with H_{c2}, the upper field required for $-4\pi M=0$ (compare Fig. 1 and Fig. 2).

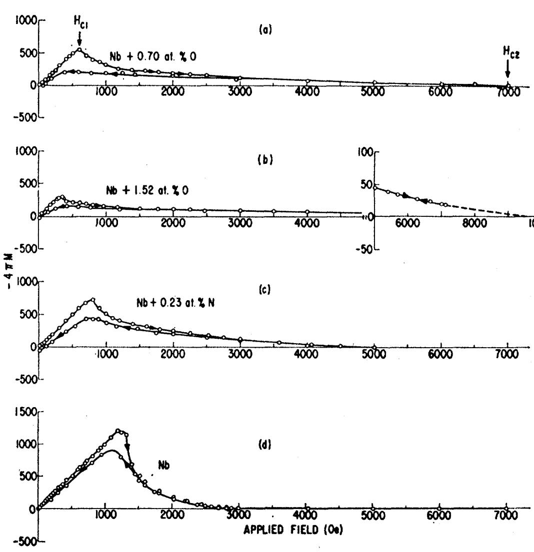


FIG. 2. Magnetization characteristics at 4.2°K of niobium and niobium containing interstitial solutes of oxygen and nitrogen (0.030-in. diam wires).

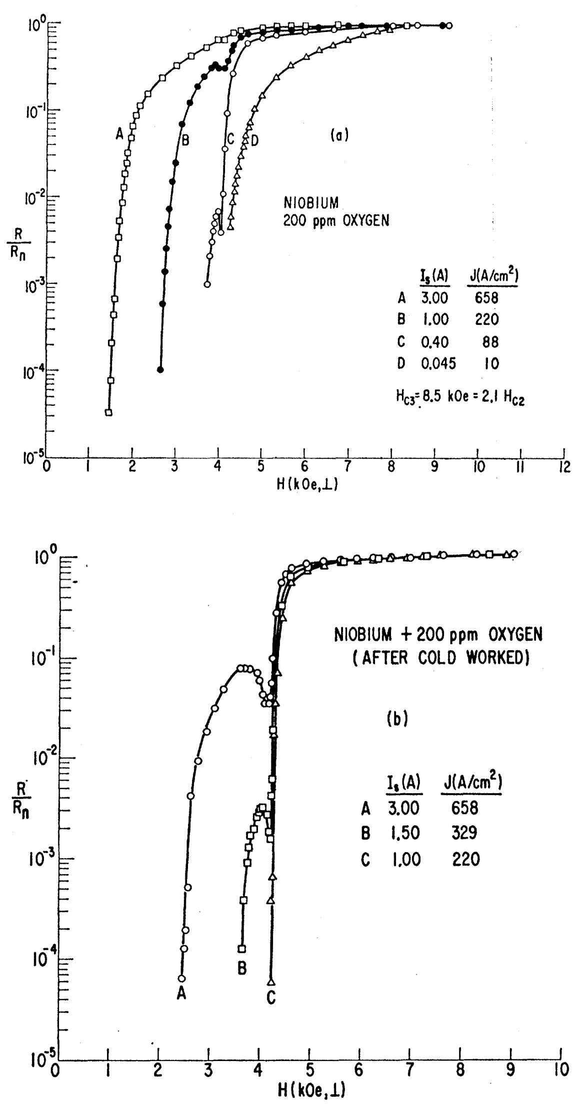


FIG. 3. The resistive transition R/R_n as a function of applied field at 4.2°K for a niobium wire containing 200 ppm oxygen (a) before cold worked diam=0.030 in.), H_{c3} evaluated at $J=10$ A/cm² and (b) after cold worked by hammering (diam ≈0.027 in.). $H_{c3}=8.0$ kOe$=1.9\,H_{c2}$ at $J=200$ A/cm².

For niobium outgassed and annealed, no apparent discontinuities in the transition are seen even at low current densities [Fig. 1(d)]. At these small J values the noise level in R/R_n is greater than 1×10^{-3}. However, the anomaly can still be observed in niobium containing as little as 200 ppm oxygen [Fig. 3(a) and (b)]. When the oxygen is beyond the solubility limit

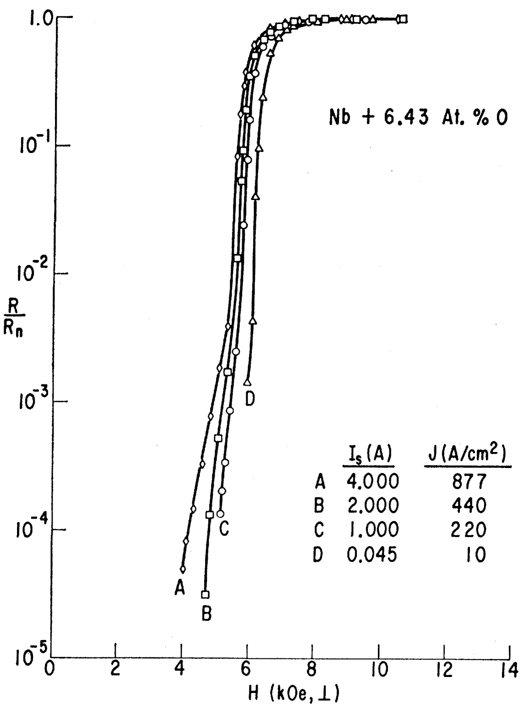


FIG. 4. The resistive characteristics R/R_n as a function of current density and applied tranverse field at 4.2°K for a niobium wire (0.030-in. diam) containing oxygen concentration [6.4 at.% oxygen plus some nitride contamination revealed by micrograph and x-ray studies (Ref. 2)] beyond the solubility limit at the temperature of introduction.

at the temperature of introduction,[13,14] no resistance minima are apparent (Fig. 4).

The magnetization behavior of these interstitial solid solutions,[2] and Nb,[15] is that of a Type II superconductor. In such a superconductor, the total surface energy becomes negative at H_{c1} and a "mixed state" ensues. As the field is increased beyond H_{c1}, the flux penetration increases until at H_{c2} the transformation to the normal state is achieved. The model is based on the material being homogeneous and defect-free, exhibiting reversible magnetization characteristics. It is believed that the resistance $R(H)$ in the "mixed state" is associated with flux motion or creep of the kind discussed by Kim, Hempstead, and Strnad,[16] i.e., resistance is determined from the rate at which flux filaments are moving. Based on this model, increasing the interstitial concentration seems to increase the flux motion for a given J since R increases [compare Fig. 1(a) and 1(b)]. When the solubility limit of the interstitial is exceeded, no resistance appears below H_{c2} within the limits of the measurements (compare Fig. 4 and Fig. 9, Ref. 2). In the "mixed state" the interaction of defects, inhomogeneities, or precipitates with flux filaments controls the hysteresis of the type described by Bean[17,18] and the equivalent critical current.[16,19]

Anderson and Kim[20] have suggested a possible explanation of the anomalous resistance drop after an initial rise based on the flux-creep model. As H_{c2} is approached, the lattice flux lines are expected to become more rigid, slowing down the rate of flux motion. Oxygen and nitrogen present in small concentrations would tend then to favor this process.

Above H_{c2} the variations in resistivity appear at smaller current densities dependent on the measuring currents. R approaches R_n at H_{c3}, the field at which the material is completely normal. There are two possible explanations for the variation of the $R(H)$ curve in this region. One is that recently proposed by Saint-James and de Gennes[21] envisioning a superconducting sheath along parts of the sample which disappears at H_{c3}. Recently, experimental evidence[22–24] has appeared showing that this remanent superconductivity is basically a surface effect in agreement with this point of view. Some supporting evidence for this is also presented in this work (see below). An alternative explanation may be that above H_{c2} a real resistance occurs; and that the shape of this portion of the $R(H)$ curve manifests the destruction of the final traces of superconductivity due to lattice irregularities such as dislocations, grain boundaries, and inhomogeneities having a higher critical field than the matrix. The connected regions would play an important role near and just above H_{c2}, while the discontinuous superconducting regions would be responsible for the shape of the curve at the top of the transition.

2. *Influence of the Interstitial on H′*

The field at which the resistivity first becomes detectable H' decreases for these specimens as the current in the wire increases (Fig. 5). It appears to reach a limiting value corresponding to the value H_{c1}, obtained from the magnetization curve (Fig. 2). In this curve, H_{c1} is the field at which the flux first penetrates the specimen. In this comparison the applied

[13] A. U. Seybolt, Trans. AIME **200**, 774 (1954).
[14] E. Gebhardt and R. Rothenbacher, Z. Metalk. **54**, 623 (1963).
[15] T. F. Stromberg and C. A. Swenson, Phys. Rev. Letters **9**, 370 (1962).
[16] Y. B. Kim, C. F. Hempstead, and A. R. Strnad, Phys. Rev. **131**, 2486 (1963).
[17] C. P. Bean, Phys. Rev. Letters **8**, 250 (1962).
[18] J. Silcox and R. W. Rollins, Appl. Phys. Letters **2**, 231 (1963).
[19] J. Friedel, P. G. de Gennes, and J. Matricon, Appl. Phys. Letters **2**, 119 (1963).
[20] P. W. Anderson and Y. B. Kim, Rev. Mod. Phys. **36**, 39 (1964).
[21] D. Saint-James and P. G. de Gennes, Phys. Letters **7**, 306 (1964).
[22] G. Bon Mardion, B. B. Goodman, and A. Lacaze, Phys. Letters **8**, 15 (1964).
[23] C. F. Hempstead and Y. B. Kim, Phys. Rev. Letters **12**, 145 (1964).
[24] W. J. Tomasch and A. S. Joseph, Phys. Rev. Letters **12**, 148 (1964).

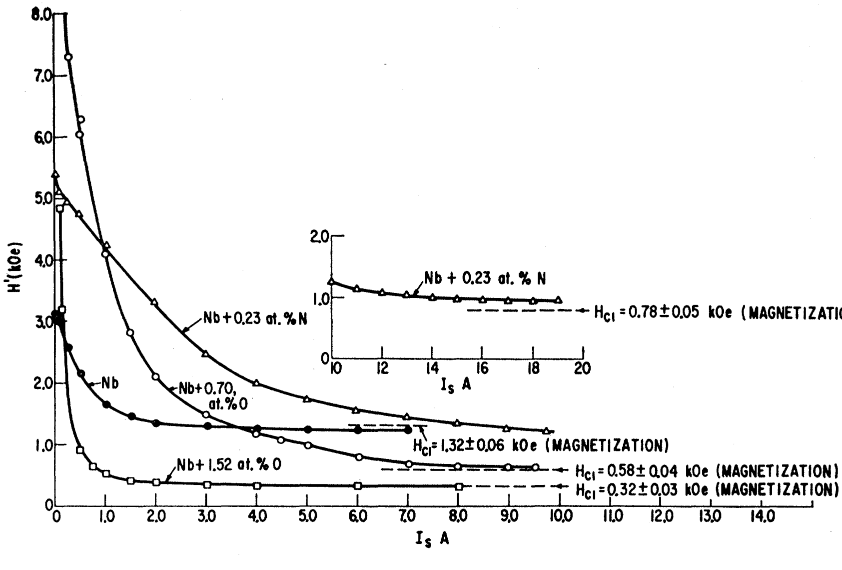


FIG. 5. The transverse field H' required for the initial appearance of resistance ($R/R_n \lesssim 1\times10^{-3}$) at 4.2°K as a function of specimen current I_s (amperes). The values of H_{c1} are evaluated from the magnetization curve.

field value does not contain the small correction due to the magnetic field generated by the current in the wire. H' decreases as the interstitial solute concentration increases. The resistive transition occurring between H' and the field at which the resistance minimum occurs, H_{c2}, for a given J becomes broader as the solute concentration increases [compare Figs. 1(a) and 1(b)]. More quantitative comparisons should be done at the same reduced temperature since oxygen present interstitially lowers the transition temperature.[2]

3. *Critical Current Density*

The critical current density J_c as a function of transverse field, of wire specimens of annealed niobium and annealed niobium containing various concentrations of oxygen is shown in Fig. 6. J_c extends to higher fields as the oxygen concentration increases. This is no longer true when the solubility limit is exceeded. A comparison of the curves with their respective magnetization data (Fig. 2) clearly defines three portions: (1) below H_{c1}, a sharp decrease in $J_c(H)$ takes place analogous to the behavior in a "soft" superconductor; (2) the "mixed state" region between H_{c1} and H_{c2}, where the anomalous behavior in the threshold-field curve (peak effect) related to the resistance minimum discussed above is evident in the niobium containing 0.70 at.% oxygen and (3) a region above H_{c2}.

Below H_{c1}, one assumes that the transport current J is carried in a thin shell (London penetration depth). Between H_{c1} and H_{c2}, it is believed that the transport current is controlled by the interaction of defects and flux filaments and that the net flow of current is dependent on the concentration gradient of flux filaments resulting from this interaction. J_c is determined as soon as the motion of the flux filaments is detected.[16,19]

Above H_{c2}, evidence cited below seems to indicate that current could be carried by a superconducting layer as suggested by Saint-James and de Gennes.[21] An alternative explanation could be that starting at H_{c2}, the continuous supercurrent flux filaments in the main body of the matrix no longer exist and the current carrying mechanism changes to that associated with extended defects consisting of higher critical field superconducting structural defects or physical filaments. Similar suggestions have been made earlier (e.g., see

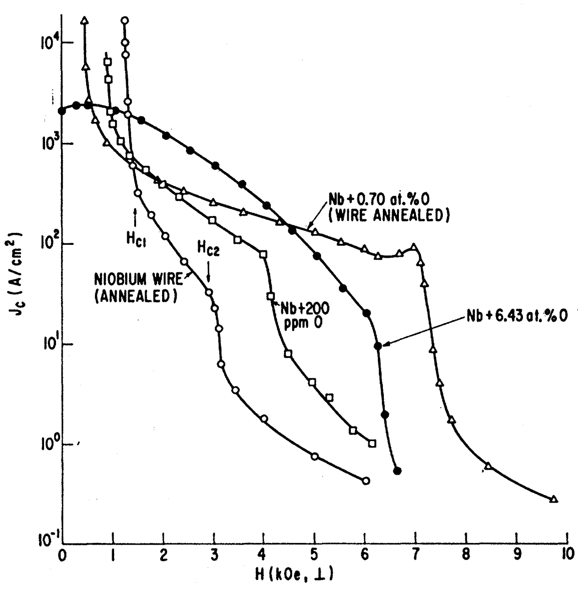


FIG. 6. Threshold current density-field behavior of some annealed niobium wires (0.030-in. diam) containing various amounts of oxygen. Annealed and outgassed niobium is also shown for comparison ($T=4.2$°K).

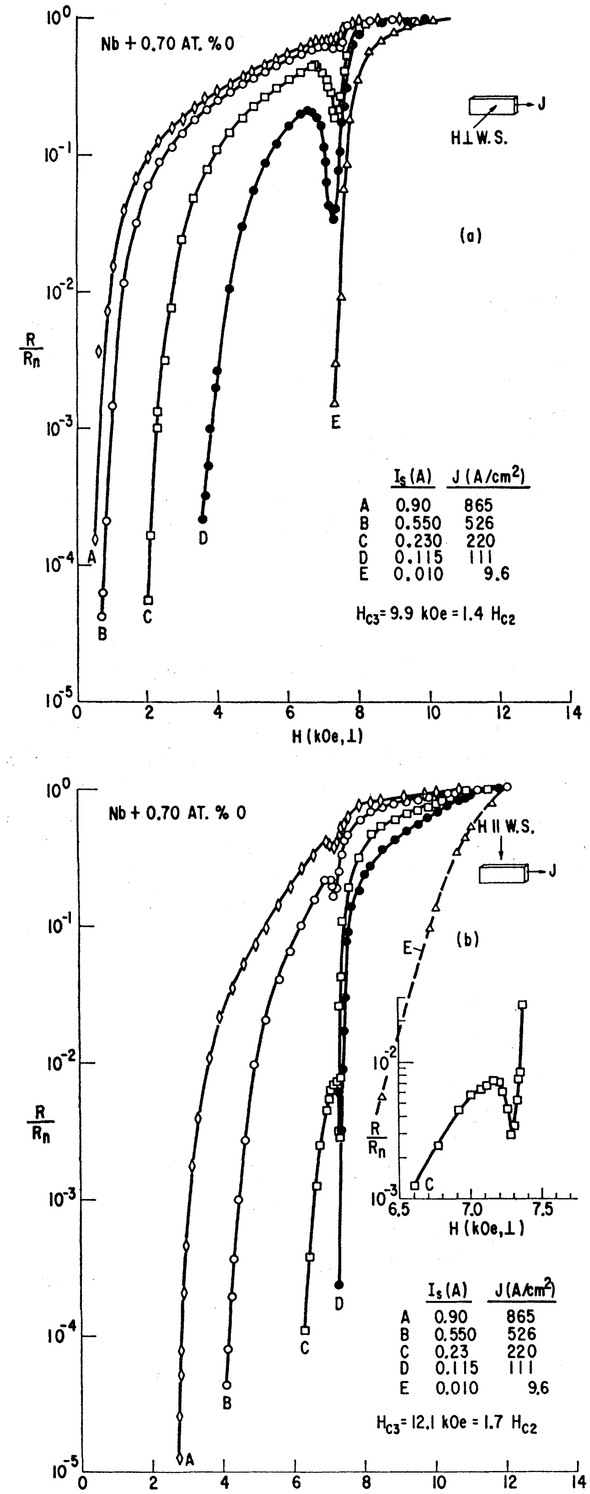


FIG. 7. The resistance characteristics R/R_n as a function of applied transverse field at 4.2°K for an annealed ribbon of niobium (0.032×0.007 in.) containing 0.70 at.% oxygen (a) with field perpendicular to the wide side ($H\perp$w.s.); (b) with field parallel to the wide side ($H\|$w.s.). H_{c3} values are evaluated at $J\simeq10$ A/cm^2.

discussion Ref. 25). $J_c(H)$ drops off rapidly in this region since the superconducting paths would, presumably, not be continuous nor necessarily be characterized by a uniform critical field. One would expect the rate of decrease of $J_c(H)$ to depend on the concentration and nature of the defects.

For the specimens containing oxygen in concentrations exceeding the solubility limit at the temperature of introduction, the critical current has a relatively lower value at zero field, remaining almost constant as the field is increased, decreases monotonically and then sharply at a field approximately corresponding to that where the magnetization becomes zero ($B=H$) (see Fig. 9, Ref. 2). For this specimen H_{c1} and H_{c2} cannot be clearly identified from the magnetic behavior since it exhibits pronounced magnetic hysteresis. At intermediate field the current density is somewhat higher than that of Nb and dilute Nb-O solutions indicating perhaps some more effective interaction of the precipitates with flux filaments in the Nb matrix.

B. Influence of Field Orientation

1. Resistive Transition at Constant Current Density

a. Nb+0.70 at.% Oxygen-Annealed Ribbon. Figures 7(a) and 7(b) show the resistance transition of an annealed niobium ribbon containing 0.70 at.% oxygen for $H\perp$w.s. and $H\|$w.s., respectively. $R(H)$ in the mixed state for a given J is lower than for the wire specimen [see Fig. 1(a)]. Of the two field orientations, it is smaller when $H\|$w.s. The anomalous resistance minimum is also smaller for this field direction. While H_{c2} is independent of field direction, H_{c3} has a higher value when $H\|$w.s. In either case, H_{c3} tends to decrease as J increases. If H_{c3} is evaluated at the smallest J, namely $J=10$ A/cm^2, the ratio $H_{c3}/H_{c2}=1.68$, when H is parallel to the wide side. This value is in good agreement with the Saint-James and de Gennes analysis[21] which predicts $H_{c3}/H_{c2}=1.695$, when H is parallel to the surface. For H perpendicular to the surface, the Saint-James and de Gennes analysis reduces to that of Abrikosov with no remanent superconductivity expected beyond H_{c2}. In this study when the field is perpendicular to the wide side of the annealed ribbon [Fig. 7(a)] some remanent superconductivity does exist and $H_{c3}/H_{c2}=1.37$ ($J=10$ A/cm^2). The ratio is smaller than the theoretical value, although the edges of the ribbon specimen provide some surface parallel to the field.

b. Nb+0.70 at.% Oxygen-Cold-Worked Ribbon. When a ribbon, the same geometry as that above, is made by cold-working niobium wire containing 0.70 at.% oxygen (i.e., wire uniformly compressed to a flat ribbon) there occurs a decrease in the resistance in the mixed state and an enhancement of the resistance

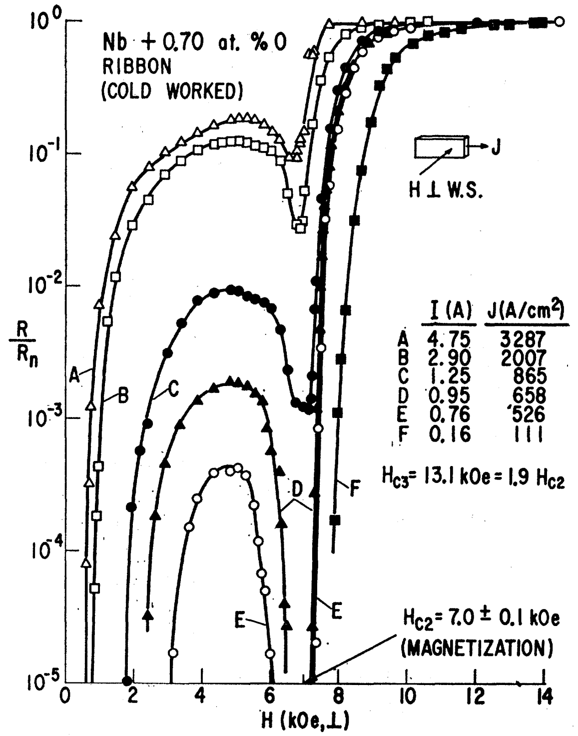
[25] W. DeSorbo, Rev. Mod. Phys. 36, 90 (1964).

minimum for either of the two field directions when compared with the results obtained on the annealed specimen [compare Fig. 7(a) with 8(a) and 7(b) with 8(b)]. The resistance decrease is more pronounced when $H\|$w.s. of the ribbon. This decrease in $R(H)$ in the mixed state upon cold working is consistent with the point of view[16] that R is determined from the rate at which flux filaments are moving. Increasing dislocation (or defects) and/or segregation and precipitate concentration impedes the motion decreasing R. The Nb–O solutions, as prepared, are all supersaturated at room temperature (equilibrium solubility at room temperature is vanishingly small.)[13,14] Upon cold working, the dislocations can help take oxygen out of solution since they can serve as sites for segregation and precipitation and provide paths for enhanced diffusion.

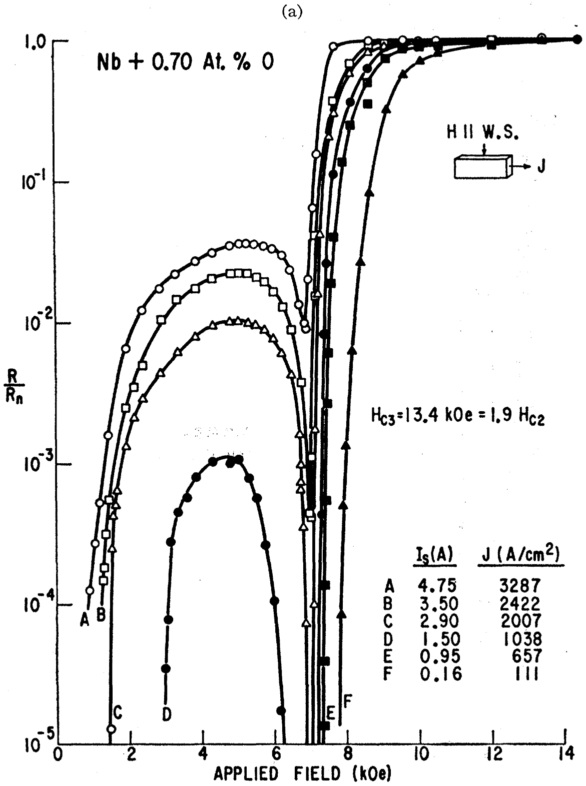
The resistive anomaly and its enhancement by cold work may be related to the relative orientation between the flux filaments in the mixed state and defects with that of the field.[26] On the basis of the Anderson and Kim[20] suggestion, flux line rigidity would not only increase near H_{c2} with cold work, but it would also be anisotropic. With the type of deformation used in this work, this relative orientation would be expected to be a complex one. The demagnetization coefficient itself seems to be important in the low-field region. The small change, if any, of H_{c2} upon cold work (see Fig. 9) implies, from the Abrikosov model, that the mean free path of the bulk specimen has not been altered appreciably and that possibly only a small fraction of the total solute atom segregating to defects are responsible for the large changes in the resistive characteristics observed in the mixed state. The small changes in H_{c2} with cold work accompanied by large changes in magnetization peak and hysteresis loop are consistent with earlier observations made on some lead-base alloys.[27]

For cold-worked ribbon, H_{c3} is larger than that observed on the annealed ribbon, and the ratio H_{c3}/H_{c2} equals 1.91 ($J=111$ A/cm^2) for either field direction [see Figs. 8(a) and (b)] and is expected to be even larger for smaller J. The increase in H_{c3} is anticipated if defects participate in the nucleation to the superconducting sheath as suggested by Saint-James and de Gennes. The distinction in $R(H)$ between parallel and perpendicular field orientations for the cold worked ribbon is less apparent in the region H_{c2} to H_{c3} [compare Figs. 8(a) and (b)]. These observations are in agreement with similar results recently reported by Hempstead and Kim[23] on some substitutional solid solutions of Type II superconductors.

c. Dependence of H'—Nb+0.70 at.% Oxygen (An-



(a)



(b)

FIG. 8. The resistance characteristics R/R_n as a function of applied transverse field at 4.2°K for a cold-worked ribbon (0.032×0.007 in.) containing 0.70 at.% oxygen (a) with field perpendicular to wide side; (b) with field parallel to the wide side. H_{c3} values were evaluated at $J=111$ A/cm^2.

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[26] Anisotropic effects observed in current density-field studies of some substitutional alloys [J. J. Hauser and R. G. Treuting, Phys. Chem. Solids 24, 371 (1963)] have been related to the presence of an "anisotropic filamentary structure" produced by cold rolling and not specifically to changes in the demagnetization coefficient.

[27] J. D. Livingston, Phys. Rev. **129**, 1943 (1963).

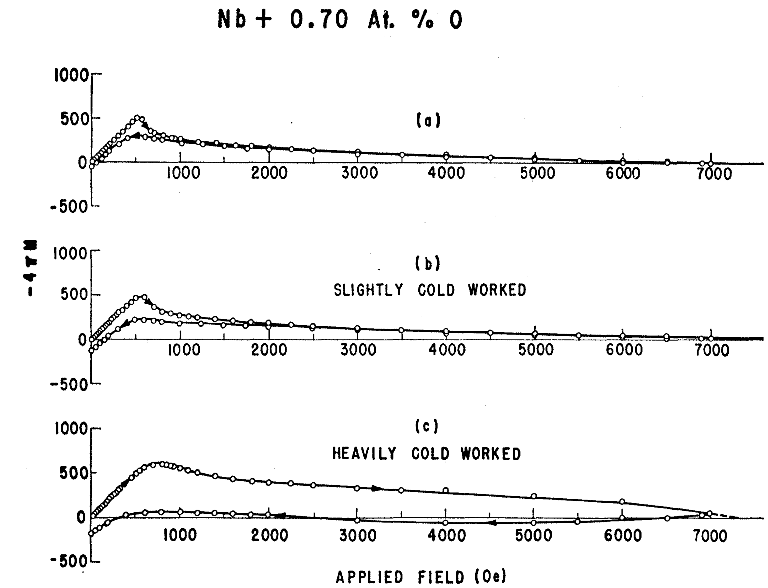


FIG. 9. The influence of cold work on the magnetization behavior at 4.2°K of niobium +0.70 at.% oxygen (a) 0.030-in. diam wire, (b) same wire with diameter reduced to ~0.027 in. by hammering, and (c) wire after uniformly compressed to flat ribbons 0.032×0.007 in.

nealed and Cold-Worked Ribbons). Changes in H' as a function of sample current corresponding to cold worked and to annealed specimens for the two-field orientations mentioned above are presented in Fig. 10.

d. Niobium Ribbon—Outgassed and Annealed. Annealed niobium ribbon, whose interstitial concentration is less than 5 ppm, does not exhibit the resistance anomaly when the field orientation is either perpendicular or parallel to the wide side [Figs. 11(a) and (b)]. The resistance in the mixed state below H_{c2} (see also Fig. 12 for H_{c2} evaluated from the magnetization data) is larger when the field is perpendicular to the wide side.

Above H_{c2}, the resistance is smaller when $H\|$w.s. of the ribbon. This could be due to the existence of a superconducting sheath predicted for this field orienta-

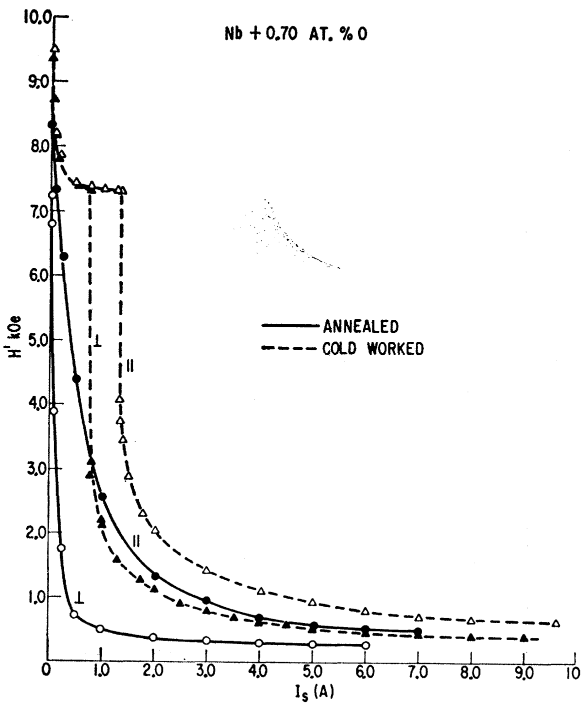


FIG. 10. The transverse field H' required for the initial appearance of resistance ($R/R_n<1\times10^{-3}$) at 4.2°K as a function of specimen current, I_s (amperes) for (a) annealed and (b) cold-worked ribbon of Figs. 7 and 8.

TABLE I. The influence of oxygen concentration in niobium wires (0.030-in. diam) on the ratio H_{c3}/H_{c2} at 4.2°K (see note added in proof). Magnetic field perpendicular to wire and to flow of current.

	T_c(°K) (Ref. 2)	H_{c2}[a] (kOe)	K[b]	H_{c3}/H_{c2} ($J=10$ A/cm²)
Nb				
wire	9.4_6	2.70	1.24	2.5_2
ribbon $H\|$w.s.	9.4_6	2.70	1.24	2.4_4
ribbon $H\perp$w.s.	9.4_6	2.70	1.24	1.9_0
Nb+200 ppm O wire				2.0_0
Nb+0.7 at.%O				
wire	8.7_8	7.0	3.64	1.6_0
ribbon $H\|$w.s.	8.7_8	7.0		1.6_8
ribbon $H\perp$w.s.	8.7_8	7.0		1.3_7
Nb+1.52 at.%O wire	8.0_4	9.6	6.03	1.2_1
Nb+6.4 at.%O wire	~9.0			<1.2

[a] Determined magnetically.
[b] For value of H_c used to evaluate K, see Ref. 2.

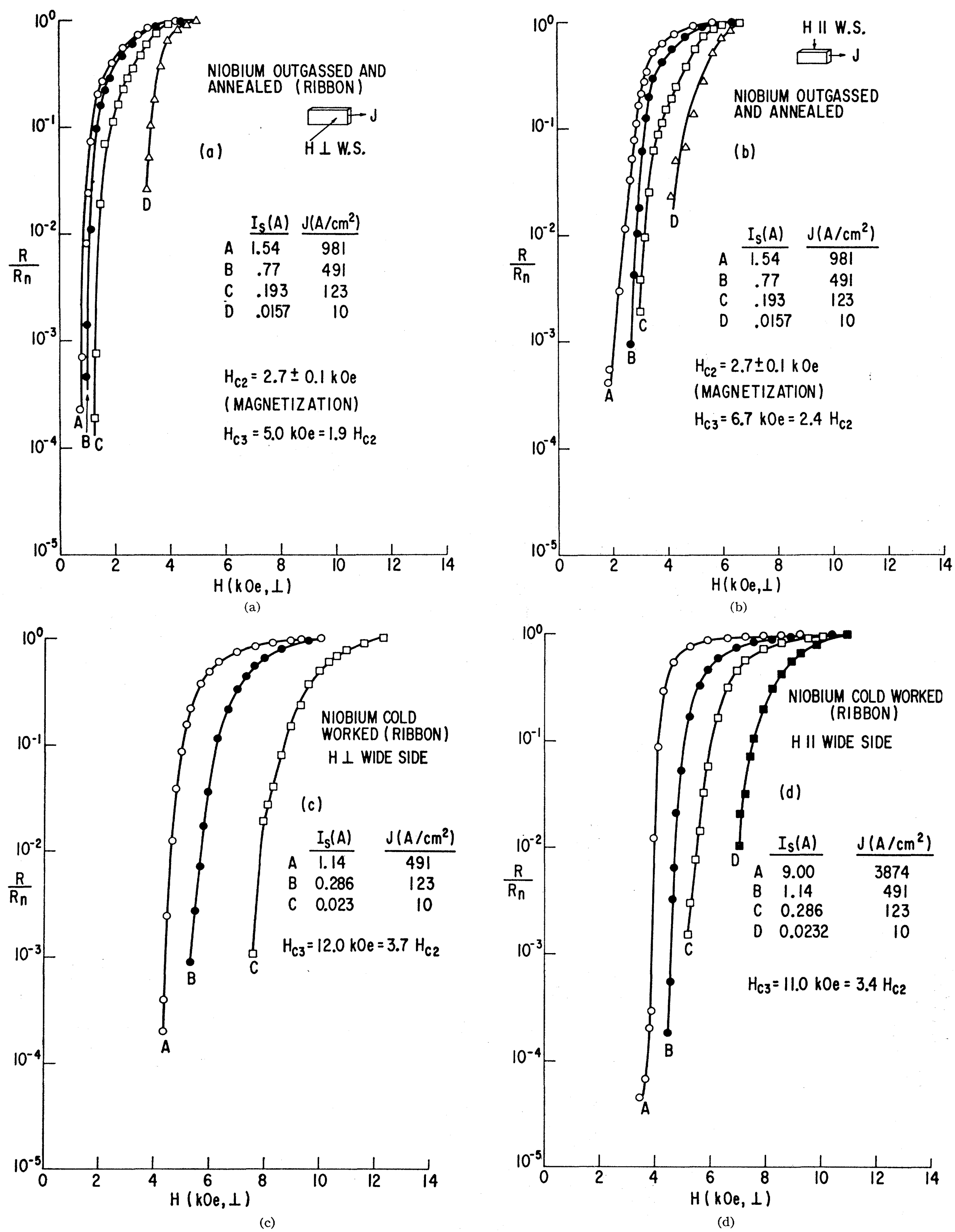


FIG. 11. The resistive characteristics R/R_n as a function of applied transverse field at 4.2°K for niobium ribbons (0.032×0.007 in.) containing less than 5 ppm interstitials: (i) annealed; (a) field perpendicular to wide side (b) parallel to wide side; (ii) cold worked by uniformly compressing a 0.030-in. diam wire (ribbon diamensions 0.032×0.007 in.); (c) field perpendicular to wide side; and (d) field parallel to wide side. H_{c3} values are evaluated at $J \cong 10$ A/cm².

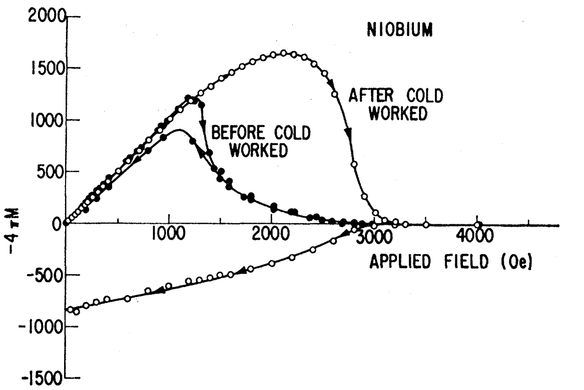


FIG. 12. The influence of cold work on the magnetization characteristics of niobium containing less than 5 ppm oxygen content for an annealed specimen (0.030-in. diam wire) and the same specimen cold worked by compression (ribbon 0.032×0.007 in.) $T=4.2°K$.

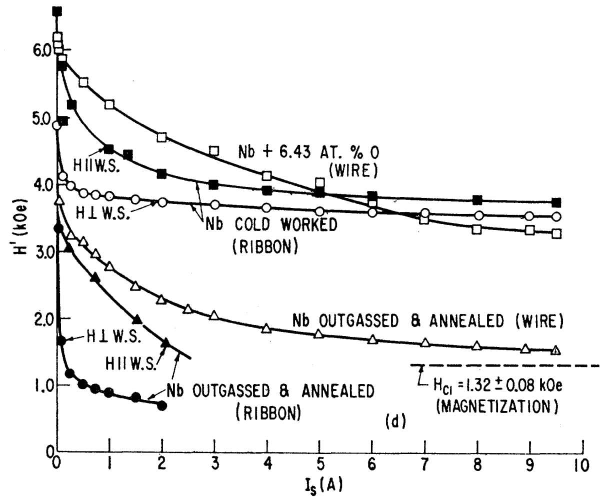


FIG. 13. The field H' at which the resistivity first appears as a function of current is summarized for Nb ribbons shown in Fig. 11. The results for Nb+6.4 at.% O (wire 0.032-in. diam) are also shown ($T=4.2°K$).

tion.[21] However, the ratio H_{c3}/H_{c2} is equal to 2.44 ($J=10$ A/cm^2) which is larger than the theoretical value (see note added in proof). It is interesting to note that for pure niobium $K(=H_{c2}/\sqrt{2}H_c)$ is small compared to the values observed in the Nb–O solutions (see Table I). For $H\perp$w.s., $H_{c3}/H_{c2}=1.85$ ($J=10$ A/cm^2) smaller than that observed for the parallel field orientation but still larger than the theoretical value (see note added in proof).

e. Niobium Ribbon—Outgassed and Cold Worked. For the cold-worked ribbon, whose interstitial concentration is less than 5 ppm, $R(H)$ [see Fig. 11(c) and (d)] could not be detected below H_{c2} (Fig. 11) within the limits of the measurements. Again, such results are in agreement with the notion that in the mixed state, $R(H)$ is dependent on the rate of motion of flux filaments.[16] In niobium with low interstitial concentration the dis-

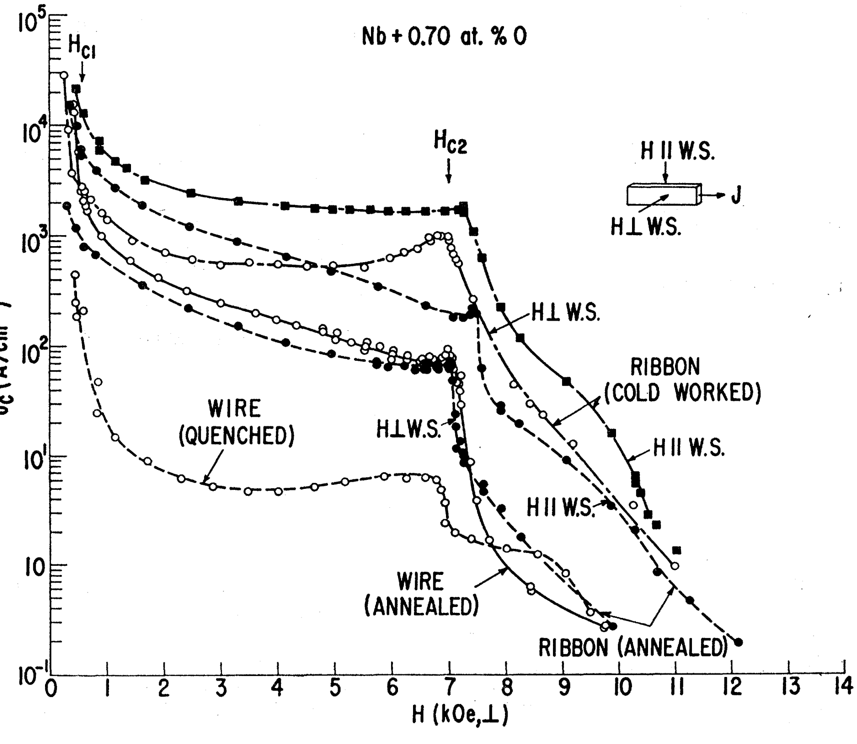


FIG. 14. Threshold current-density field behavior of several specimens of niobium wire (0.030-in. diam) and ribbons (0.032×0.007 in.) containing 0.70 at.% oxygen at 4.2°K. H_{c1} and H_{c2} determined from magnetization data.

locations are effective in reducing this rate. In these cold-worked ribbons H_{c3} and the ratio H_{c3}/H_{c2} are larger than the corresponding values observed in annealed ribbons. Again, the distinction between the field orientation of the resistance transition is less significant, similar to the behavior in cold-worked Nb–O ribbons.

f. H' Dependence on Field Orientation in Niobium (Ribbon). The field H' at which the resistivity first appears as a function of sample current is summarized in Fig. 13 for annealed and cold-worked niobium. The limiting value of H' at high current approaches H_{c1} for the annealed wire. For the annealed ribbon, the limiting value may be smaller than H_{c1} for either field direction, while for cold-worked ribbon it is larger than H_{c1}. For comparison, the results are also shown for niobium containing oxygen beyond the solubility limit at the temperature of introduction. H' for this material is large as in cold-worked Nb.

2. *Critical Current Density—Annealed and Cold-Worked Nb and Nb+0.70 at.% Oxygen*

The threshold current-field data $J_c(H)$ for cold-worked ribbons of both Nb+0.70 at.% oxygen and Nb are summarized in Figs. 14 and 15, respectively, where they are compared with the data obtained on similar but annealed ribbon specimens. The data on annealed wire specimens are also shown for comparison. The values of H_{c1} and H_{c2} were obtained from the magnetization data. Cold working increases the critical current carrying capacity in the mixed state in both materials by introducing dislocations. These play a role in stabilizing the flux filaments in the mixed state reducing $R(H)$. In Nb-O solutions, some segregation and precipitation at these dislocations may be participating in this process.

The anomolous increase in $J_c(H)$ curve (peak effect) related to the resistance minimum, discussed above, is evident in the interstitial solid solution even before cold work (Fig. 14). This is in contrast to the behavior in substitutional solid solutions where it is usually necessary to cold work the material to bring out the anomaly where it also occurs at H_{c2}.[25] However, upon cold working these interstitial solutions (ribbons), the peak is enhanced when the field is perpendicular to the wide side, always coincident with smaller J_c values in the mixed state below H_{c2}. For this same material the peak virtually disappears when the field is parallel to the flat surface, but $J_c(H)$ is now larger in the mixed state. Mendelssohn (see discussion of Ref. 25) attributes the peak effect, occurring only in the transverse field, to a more favorable relative orientation assumed by the direction of the superconducting paths and the field as H_{c2} is approached (see also Hauser and Treuting, Ref. 26). An alternative explanation is that proposed by Anderson and Kim[20] (see above). In either outgassed or cold-worked niobium no anomalous variation is evident in the $J_c(H)$ curve for either of the two field orientations used to examine the ribbons (Fig. 15).

Above H_{c2} field orientation effects on $J_c(H)$ are quite evident for both Nb+0.70 at.% oxygen and Nb after each has been annealed (see Fig. 14 and 15, respectively). The ribbon specimens show a greater ability to carry superconducting current when the field is parallel to the surface which would be expected from the Saint-James and de Gennes model.[21] In cold-

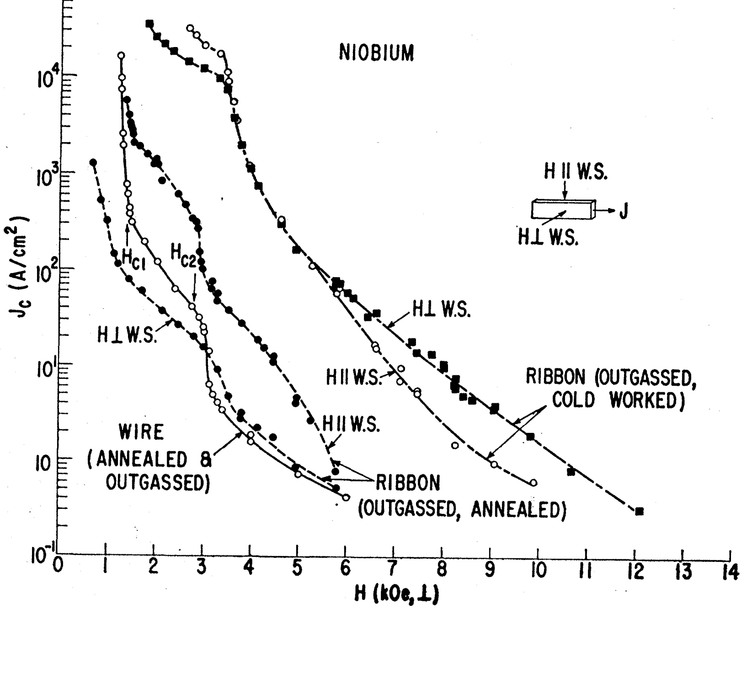


FIG. 15. Threshold current density-field behavior of several wire (0.030-in. diam) and ribbon (compressed to 0.030×0.007 in.) specimens of niobium, each containing less than 5 ppm interstitial concentration, showing the influence of cold work and field direction ($T=4.2°$K).

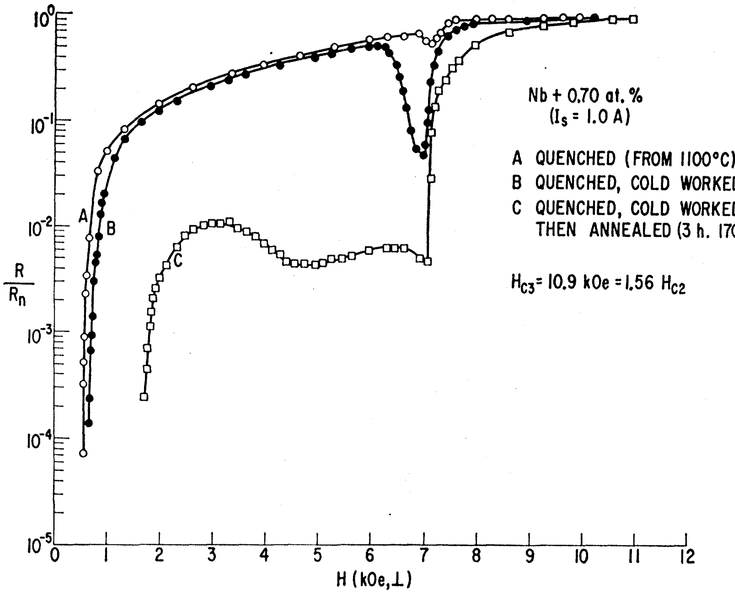


FIG. 16. Resistance characteristics R/R_n of a wire specimen (0.030-in. diam) of Nb+0.70 at.% oxygen; (a) quenched in helium exchange gas from an homogenization temperature 1100°C to room temperature; (b) quenched and cold worked by uniform compression roughly to a rectangular form approximately 0.028×0.032 in.; (c) after (b) the same wire was given a low temperature anneal, 3 h at 170°C (J=220 A/cm²) (T=4.2°K). At this current density $H_{c3}=10.9=1.56$ H_{c2}.

worked ribbons the field orientation effect on $J_c(H)$ is smaller and for Nb ribbon it is nonexistent just below H_{c2} with the deviations going over into the opposite direction for small $J_c(H)$ values. Similar results have been observed in cold-worked Nb+3 at.% Ti.[25] These results corroborate the dependence of resistance on field orientation above H_{c2} described above. As the defect concentration increases, the distinction between $R(H)$ for ∥ and ⊥ field orientation becomes less significant.

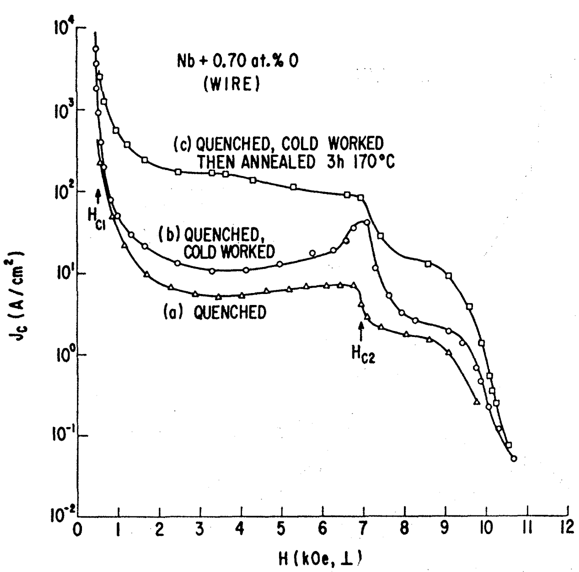


FIG. 17. Threshold current-density field behavior of the same specimens shown in Fig. 16 (T=4.2°K).

C. Ratio H_{c3}/H_{c2} and Oxygen Concentration in Niobium

The ratio H_{c3}/H_{c2} observed on annealed niobium wires containing various concentrations of oxygen are summarized in Table I. The values are approximately equal to those observed on ribbon samples when H∥w.s. (e.g., Nb and Nb+0.70 at.% oxygen). The ratio is largest for pure niobium which also has the lowest K. It decreases with increasing K and increasing solute concentration (see note added in proof).

D. Strain Aging Nb+0.70 at.% Oxygen

Some preliminary experiments have been carried out to vary the degree of interstitial segregation to dislocations. This was done by studying both $R(H)$ and $J_c(H)$ on a wire specimen, Nb+0.70 at.% oxygen, (a) quenched, (b) then cold worked, and (c) annealed at 170°C for 3 h in a pressure less than 1×10^{-7} mm Hg. $R(H)$ data are summarized in Fig. 16 for $J=220$ A/cm². The resistance in the mixed state is approximately the same before and after cold working. However, the resistance anomaly in the latter is much more pronounced. Strain aging at 170°C decreases the resistance in the mixed state by a significant amount, masking out the resistance minimum.

Above H_{c2}, the data show little, if any, change in resistance upon quenching and cold work for the current density shown. The strain aging process does, however, tend to decrease R. H_{c3}/H_{c2} for the J shown is approximately 1.4_2 for these wire specimens, both before and after quenching; increasing to approximately 1.6 after strain aging.

The process of homogenizing, cold working and low

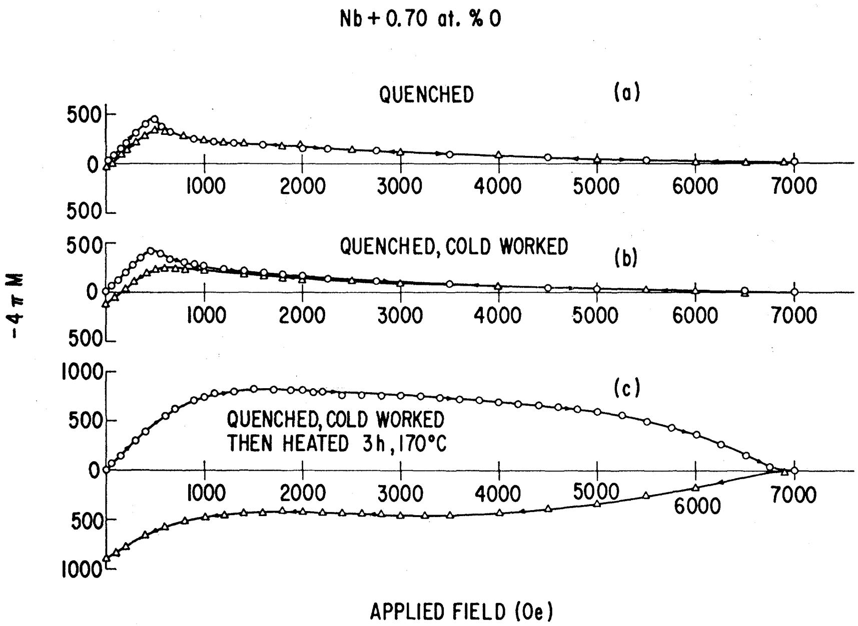


FIG. 18. The magnetization characteristics at 4.2°K of niobium containing 0.70 at.% oxygen; (a) 0.030-in.-diam wire after quenching in helium exchange gas from an homogenization temperature of approximately 1100°C; (b) a similar wire cold worked by uniformly compressing and reducing the wire to roughly a rectangle 0.040×0.019 in.; and (c) specimen (b) heated 3 h at 170°C.

temperature anneal on $J_c(H)$ and on the magnetization loop are summarized in Figs. 17 and 18, respectively. It is interesting to note that strain aging brings $J_c(H)$ in the mixed state up to where it was for slow-cooled specimens (compare Fig. 17 with Fig. 14). This result cannot be deduced from the corresponding magnetization loops (compare Fig. 16 with Fig. 8). It seems that structural changes brought about by cold working and by strain aging responsible for changes in $J_c(H)$ in the mixed state also cause changes above H_{c2} (see Fig. 17). The results indicate that in these specimens, if a superconducting sheath is carrying the current above H_{c2}, this sheath appears to be dependent on structural changes. Below H_{c1}, the current, carried in the penetration depth, appears to be independent of these changes.

The results, both $R(H)$ and $J_c(H)$, suggest that the anomalous peak effect, or resistance minimum, is strongest at some intermediate stage of the process of segregation and precipitation at dislocations. This conclusion is in agreement with the suggestion made earlier[25] that a solute or impurity atom is probably necessary for the appearance of the anomaly in both interstitial as well as substitutional solid solutions. The more wide-spread appearance of the anomaly in the former solutions has been attributed[25] to the far greater mobility (e.g., see Ref. 28) of the interstitial atom. This makes the interstitial solute atom segregate more easily to structural irregularities, such as dislocations.

As mentioned above, the anomaly is readily evident in niobium containing as little as 200 ppm oxygen, but not in Nb containing less then 5 ppm oxygen. Recent transmission electron microscopy studies[3] have shown that the presence of relatively small amounts of interstitial impurity (probably as little as 150 ppm) has a strong influence on the annealing structures of the metal. Dislocations were reported to act as sinks for interstitials present as interstitial atmospheres or precipitates. These would also tend to retard the rate of the recrystallization process and probably account for a wide variety of structures seen after high-temperature anneals. The appearance of the anomaly in niobium reported earlier[4–6] was probably due to the presence of small but significant amounts of interstitial impurities in the metal.

At present, the experimental results outline the dependence of the peak effect on various structural features, but a satisfactory theory has not been developed. Some proposed alternative explanations have been cited above. Hauser and Treuting[26] have suggested that anisotropy in defect structure is probably responsible for the minimum ("valley effect") in the $J_c(H)$ curve but reported no evidence for the presence of a second phase. Preliminary optical microscopy studies on some of the specimens reported here revealed precipitate particles only in cold-worked specimens (ribbons) occurring at a high density in certain areas presumably regions of greater dislocation density.

E. Quenching and Aging Nb+0.70 at.% Oxygen

Since strain aging at temperatures as low as 170°C has a marked effect on the mixed state, some additional experiments were carried out to study aging of quenched specimens. Some preliminary work on varying the homogenization or solution temperature, T_h was also

[28] G. B. Gibbs, D. Graham, and D. H. Tomlin, Phil. Mag. 8, 1269 (1963).

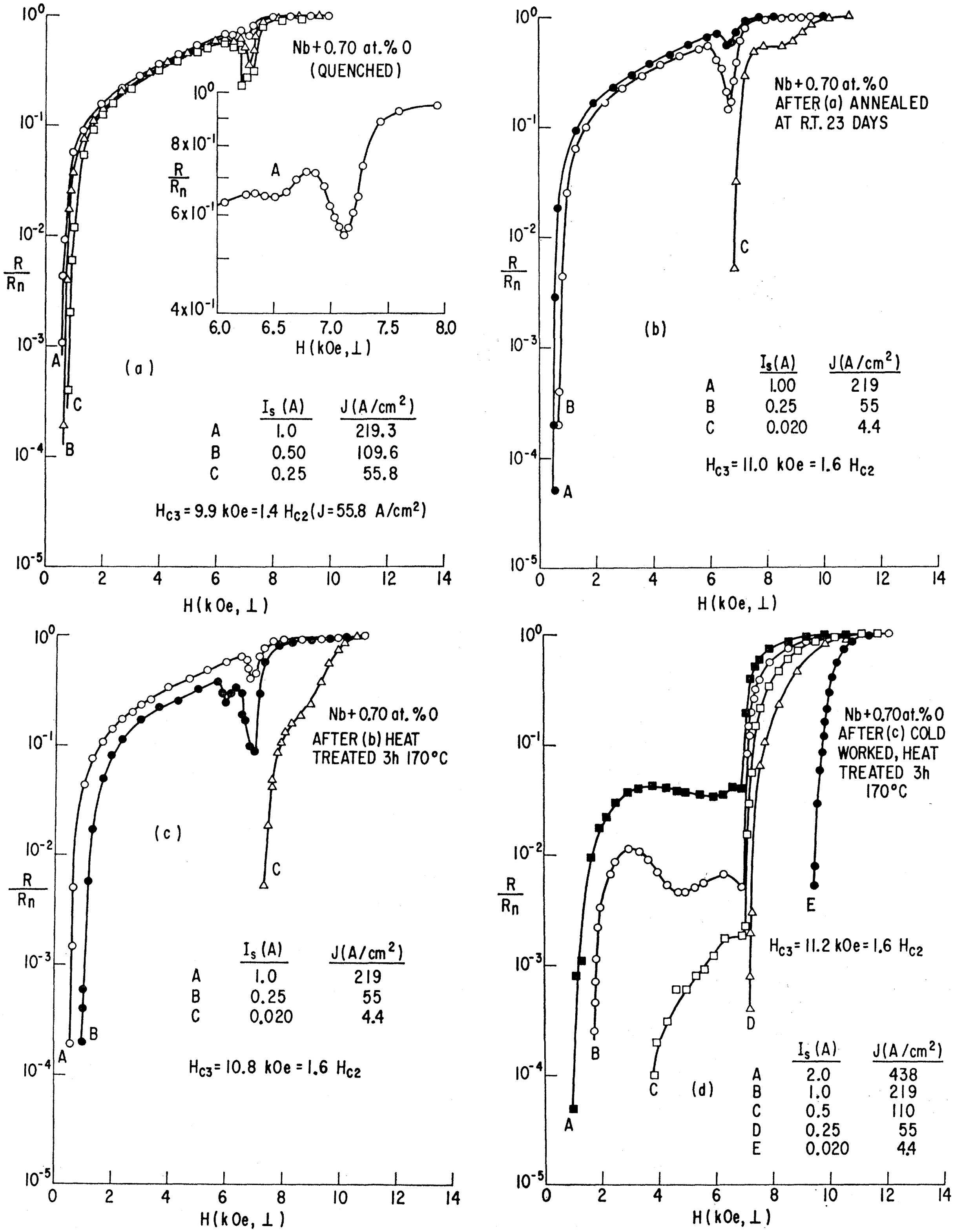


FIG. 19. The resistive transition characteristic R/R_n of niobium wire (0.030-in. diam) containing 0.70 at.% oxygen at 4.2°K; (a) after quenching in helium exchange gas from an homogenization temperature of approximately 1000°C; H_{c3} evaluated at $J=55.8$ A/cm²; (b) annealed an additional 23 days at room temperature; (c) then heated 3 h at 170°C; (d) after (c) cold work by uniform compression reducing the diameter from 0.030 in. to ~0.027 in. then heated 3 h at 170°C. In (b), (c), and (d) H_{c3} evaluated at $J=4.4$ A/cm².

attempted. In these experiments T_h was decreased to liquid nitrogen temperature in less than 20 sec.

The resistive transition of a sample Nb+0.70 at.% oxygen quenched from $T_h=1000$°C is shown in Fig. 19(a). When compared to a similar specimen cooled from the same temperature to room temperature at a slower rate (approximately 1 h) [Fig. 1(a)], it is evident that increasing the supersaturation, as well as the degree of disperseness of the solute, increases $R(H)$ in the mixed state. In the rapidly cooled specimen, a secondary dip is evident below the primary one occurring at H_{c2}. Upon aging at room temperature for 23 days, $R(H)$ remains essentially unaffected, although the secondary dip has disappeared [Fig. 19(b)]. A low temperature anneal, 3 h at 170°C, reveals a small decrease in $R(H)$, a reappearance of the secondary peak, and definite changes above H_{c2} at low current density [Fig. 19(c)]. Upon cold working the specimen and then annealing (3 h at 170°C), pronounced decreases are evident in the mixed state [Fig. 19(d)] similar to the strain aging results shown in Fig. 16.

In the region $H_{c2}\leqslant H\leqslant H_{c3}$ the process of quenching, aging, annealing, and strain aging decreases $R(H)$. Structural changes responsible for resistance changes in the mixed state are also responsible for changes observed above H_{c2}. The results again emphasize the importance of segregation and precipitation at dislocations on reducing resistance both in the mixed-state region as well as in the region above H_{c2}. If the superconducting sheath proposed for Type II superconductors[21] is responsible for the variations of $R(H)$ above H_{c2}, then the sheath is influenced by the segregation and precipitation at dislocations. However, for these wire specimens, H_{c3} ($J=4.4$ A/cm^2) appears to be unaffected by the various structural changes introduced. The ratio H_{c3}/H_{c2} remains constant with a value approximately equal to 1.6.

Upon increasing the homogenization temperature from 1000 to 1200°C and quenching rapidly, $R(H)$ in the mixed state tends to remain unchanged but the resistance minimum is now larger [compare Fig. 20(a) with Fig. 19(a)]. Increasing the homogenization temperature does not appear to change the ratio, $H_{c3}/H_{c2}=1.6$. However, in this case the resistive transitions at low current density reveal some distinct secondary minima between H_{c2} and H_{c3}. These secondary anomalies may be a consequence of some strains introduced in the wire upon cooling from higher T_h which provide new diffusion paths resulting in some regions having a slightly higher solute concentration with a corresponding higher H_{c2}. Another possibility is that these new variations are due to differences in structure that may exist at the surface and the interior of the niobium matrix when the metal is deformed a relatively small amount.[3] This different surface structure may also have a higher H_{c2}. Upon heating this specimen at 170°C for 3 h, the minima above H_{c2} disappear [Fig. 20(b)]. A relatively larger decrease in

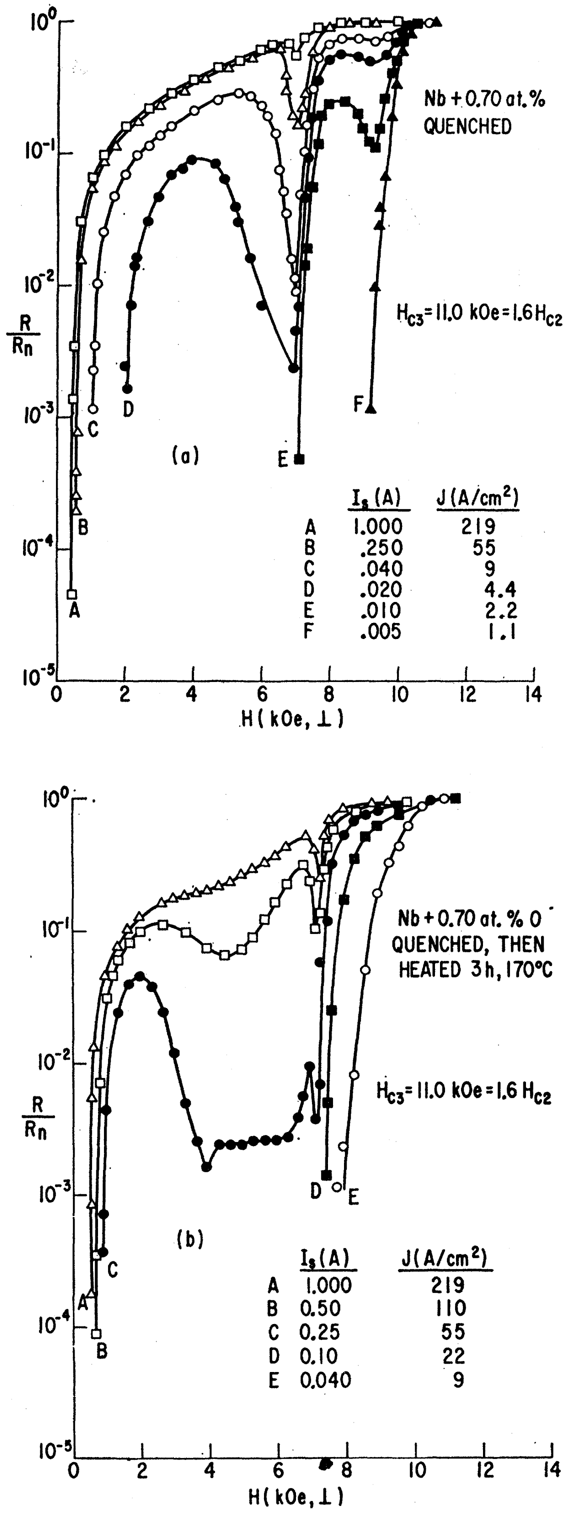
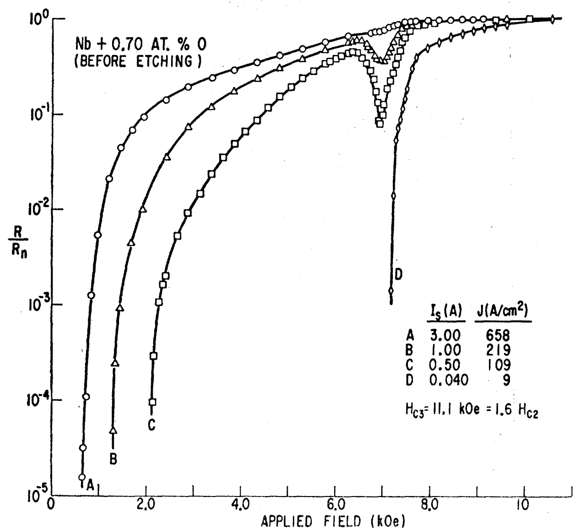
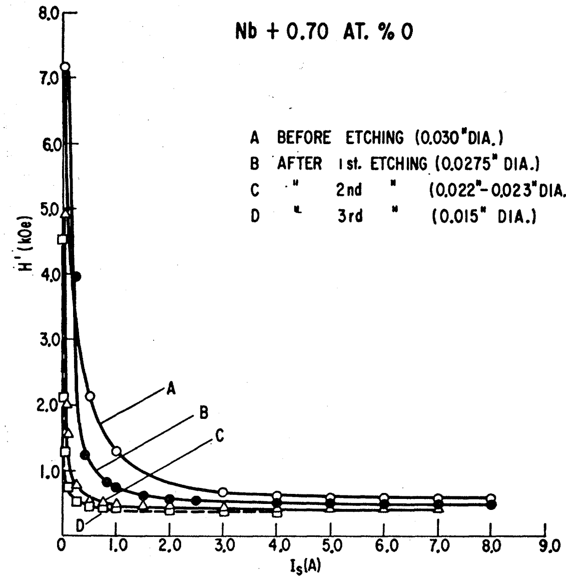


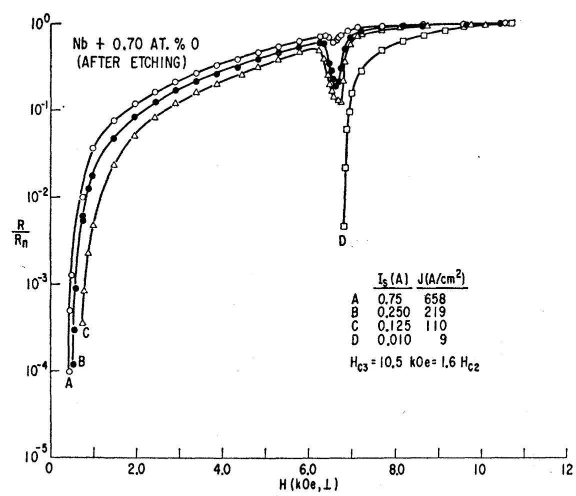
FIG. 20. The resistance characteristics R/R_n of niobium wire (0.030-in. diam) containing 0.70 at.% oxygen ($T=4.2$°K); (a) quenched in helium exchange gas from an homogenization temperature of approximately 1200°C; (b) then heated 3 h at 170°C. H_{c3} evaluated at $J=10$ A/cm^2.



(a)



(c)



(b)

FIG. 21. The resistive characteristics R/R_n as a function of applied transverse field at 4.2°K; (a) before etching specimen of niobium +0.70 at.% O, wire (0.030-in. diam); (b) after etching diameter reduced from 0.030 to 0.015 in. diam; (c) the field H' required for the initial appearance of resistance ($R/R_n \lesssim 1\times10^{-3}$) at 4.2°K as a function of specimen current I_s (amperes) before and after etching.

$R(H)$ in the mixed state, probably due to strain aging, takes place over that observed for an identical treatment given a similar specimen originally quenched from a lower T_h [compare Fig. 20(b) with Fig. 19(c)]. Note also that the value of H_{c3} or H_{c3}/H_{c2} remains unchanged.

F. Etched Specimens

The anomalous dip in the resistance transition of niobium reported earlier[6] has been known to be influenced by etching (see discussion Ref. 25). Nb–O or Nb–N specimens prepared in this work when etched with a solution consisting of 8 HNO_3, 2 H_2O, 1 HF showed only little changes in the dip characteristics even when the diameter was reduced by one half [compare Figs. 21(a) and (b)]. For example for $J=110$ A/cm^2, the field at which the minimum occurs, changes from 6.95 kOe before etching to 6.75 kOe after etching. This small decrease indicates only a small change in the average solute concentration. Assuming that changes in H_{c2} reflect average changes in solute concentration, the experiment could be useful in investigating diffusion of nonmetallic solutes in superconducting transition metals. After etching a significant increase in $R(H)$ in the mixed state, however, does occur, indicating less effective pinning of flux filaments. Above H_{c2}, the influence of etching on $R(H)$ is small or negligible. H_{c3}/H_{c2} remains unchanged and equal to approximately 1.6.

H' as a function of specimen current exhibits a decreasing trend upon reducing the wire diameter by etching [Fig. 21(b)]. Its limiting value may be smaller than H_{c1}.

SUMMARY

1. Oxygen and nitrogen as interstitial solutes in niobium cause the metal in transverse field to exhibit anomalous resistance minima or critical current maxima (peak effect). The anomaly is evident in niobium containing as little as 200 ppm oxygen but not in niobium whose interstitial concentration is approximately 5 ppm.

2. The anomaly appears at H_{c2}, the upper critical field of these Type II superconductors determined magnetically.

3. The anomaly is increased by cold working but decreased by strain aging (3 h, 170°C) and by rapid quenching. These results suggest that the anomaly is strongest at some intermediate state of the process of segregation and precipitation at dislocations.

4. The resistance (R) in the mixed state is decreased by exceeding the solute solubility limit, by cold working and by strain aging at 170°C; it is increased in the mixed state by introducing more interstitial solute, by quenching and by etching.

5. Small changes, if any, of H_{c2} upon cold work seem to indicate that only a small fraction of the total solute atom segregating to defects are responsible for large changes in both the resistive and critical current characteristics.

6. For an annealed ribbon of niobium containing 0.70 at.% oxygen ($K=3.6$) and for field orientation parallel to the wide side, H_{c3}/H_{c2} gradually increases for decreasing current density reaching a value 1.68 for $J=10$ A/cm^2, in good agreement with the predicted value of Saint-James and de Gennes. For transverse field, H_{c3}/H_{c2} is equal to 1.37.

7. For an annealed niobium ribbon containing less than 5 ppm oxygen ($K=1.2_4$) for field orientation parallel to the wide side, $H_{c3}/H_{c2}=2.44$ ($J=10$ A/cm^2), larger than the predicted value. The value is approximately equal to the ratio observed for an *annealed* niobium *wire* in a *transverse* field. Niobium wires in this field orientation show a dependence of H_{c3}/H_{c2} on oxygen concentration, varying from 2.44 for pure niobium ($K=1.2_4$) to 1.21 for niobium containing 1.52 at.% oxygen ($K=6.0_3$). It is possible that inhomogeneities in the sample where the surface is characterized by one K and the interior by another could artifically force this ratio in either direction (see note added in proof).

8. In cold-worked ribbons of niobium +0.70 at.% oxygen, or cold-worked niobium, the distinction, above H_{c2}, in $R(H)$ or $J_c(H)$ for field orientations parallel or perpendicular to the wide side becomes less significant than the corresponding values observed for annealed ribbons. Cold working increases H_{c3}/H_{c2} for either field orientation.

9. Structural changes brought about by rapid quenching, aging, strain aging responsible for changes in $J_c(H)$ or $R(H)$ in the mixed state also cause changes in the region $H_{c2}<H<H_{c3}$ but do not seem to affect the value of $H_{c3}=1.6\ H_{c2}$ for wire specimens (Nb+0.70 at.% oxygen) in transverse fields.

Note added in proof. Subsequent results carried out by the author on both pure niobium and niobium containing oxygen in concentrations below the solubility limit at the temperature of introducing oxygen show the value H_{c3}/H_{c2} is independent of κ. The value is in good agreement with the Saint-James and de Gennes theoretical value 1.695.[29]

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[29] W. DeSorbo, Bull. Am. Phys. Soc. 9, 253 (1964).