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Effect of Dissolved Gases on Some Superconducting Properties of Niobium*

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The addition of interstitial solute atoms to niobium, in concentrations below the solubility limit, lowers the transition temperature. Interstitial oxygen has the largest effect, decreasing T_c by 0.93°K per at.%; while increasing the resistivity in the normal state by 5.2 $\mu\Omega$ cm per at.%. Magnetization curves obtained on niobium ($R_{298°\mathrm{K}}/R_{10°\mathrm{K}}\approx 500$) and on similar specimens containing interstitial oxygen or nitrogen are substantially reversible and are similar to the shape predicted by Abrikosov for superconductors of the second kind. The field first penetrating the sample, H_{FP}, less than the thermodynamic critical field, H_c, decreases with increasing concentration of the interstititial atom, while H_{N}, the field at which the normal state is restored (as determined from magnetization measurements), increases. The ratio, H_{N}/H_c, is a linear function of ρ_n. When the solubility limit is exceeded, hysteresis effects become more pronounced similar to those predicted by Bean's model. Resistive measurements at low current density in longitudinal magnetic fields indicate that both niobium and its interstitial solid solutions exhibit some superconducting properties above H_{N}.

I. INTRODUCTION

THE anomalous or nonideal behavior of the so-called "hard" elemental superconductors such as niobium, vanadium, and tantalum has generally been attributed to the presence of chemical and structural impurities in the metal. Attempts to study these superconductors with small and/or controlled levels of impurity have been made only of late and much of this effort has been directed to the metal tantalum[1] where the emphasis has been primarily on interstitial additions. Earlier, Wexler and Corak[2] had investigated the superconducting properties of vanadium and the role played by the presence of small amounts of nitrogen and oxygen. However, no attempts were made initially to improve the purity of the base metal. Prior to this, Horn *et al.*[3] had made the first systematic investigation on the addition of hydrogen and nitrogen to niobium and to tantalum to form hydrides and nitrides, respectively.

Although niobium has the highest critical temperature and critical field, studies on the influences of small amounts of known impurities have been reported only recently. Hauser and Buehler[4] have cited the effect of plastic deformation in niobium on current densities in magnetic fields. The addition of substitutional metallic solutes to the transition metals including niobium and their influence on the various superconducting properties have recently been summarized.[5]

We report here some results on the superconducting properties of annealed and outgassed niobium and the effect of interstitial solute atoms, primarily, oxygen and nitrogen. This includes (a) critical temperature, T_c, (b) resistive transition characteristics of wire specimens in magnetic fields, (c) magnetic properties, and (d) critical current. The magnetization data are compared with the negative-surface-energy models[6,7] and Bean's model.[8]

II. EXPERIMENTAL

A. Preparation of Specimens

Wire specimens were made from an electron-beam melted (one-pass) ingot of niobium supplied by the Stauffer-Temescal Company, Richmond, California. Chemical analyses, carried out by D. H. Wilkins of our Laboratory, showed the following impurities in ppm: O 32, N 10, H 0.0, C 20, Ta 260, Cu<30, Fe<10, Cr<10, Ni<10, Ti<10, Si<10, B<10, Zr<500, Al<50, Mg<10, Co<10, Zn<50, Sn 30–80, In<50, Pb<10, V<10, Tl<50, Mn<10, W<200. Rods, about 0.250-in. diam were machined from the ingot then swaged and drawn to wires. The resistance ratio, $R_{298°K}/R_{10°K}$, of the wire, as received, was about 110. The annealing and outgassing procedure, as well as the subsequent quantitative addition of the interstitial solute were carried out by a procedure developed earlier by Powers and Doyle.[9] The first treatment consisted of heating the specimen, by passing a heavy current through the wire, to a temperature of about 2000°C for several hours in a residual gas pressure of less than 1×10^{-7} mm Hg. After this treatment the resistance ratio of the wire was about 280; the oxygen content was reduced to 6±3 ppm, while the nitrogen content was 5±3 ppm.[10] The criticality of temperature and residual gas pressure during the annealing and outgassing operation on the low-temperature resistivity of niobium is

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[*] See W. DeSorbo and C. E. Nichols, Bull. Am. Phys. Soc. **6**, 267 (1961); and W. De Sorbo, *ibid.* **8**, 79 (1963).

[1] For example, see D. P. Seraphim, Solid State Electron. **1**, 368 (1960); D. P. Seraphim, N. R. Stemple, and D. T. Novick, J. Appl. Phys. **33**, 136 (1962).

[2] A. Wexler and W. S. Corak, Phys. Rev. **85**, 85 (1952).

[3] F. H. Horn, W. F. Brucksch, Jr., W. T. Ziegler, and D. H. Andrews, Phys. Rev. **61**, 738 (1942); F. H. Horn and W. T. Ziegler, J. Am. Chem. Soc. **69**, 2762 (1947).

[4] J. J. Hauser and E. Buehler, Phys. Rev. **125**, 142 (1962).

[5] W. DeSorbo, Phys. Rev. **130**, 2177 (1963); J. Appl. Phys. **34**, 1378 (1963).

[6] A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **32**, 1442 (1957) [translation: Soviet Phys.—JETP **5**, 1174 (1957)].

[7] B. B. Goodman, IBM J. Res. Develop **6**, 63 (1962).

[8] C. P. Bean, Phys. Rev. Letters **8**, 250 (1962).

[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).

illustrated in Figs. 1(a) and 1(b). Wire swaged and drawn from the same ingot, but previously electron-beam melted five passes, had a resistance ratio of about 500 following the outgassing and annealing procedure. The appropriate heating temperatures for introducing the solute atoms were selected from Seybolt's[11] solubility data on oxygen in niobium and from Ang and Wert's[12] solubility data on nitrogen in niobium. Specimens whose oxygen concentration was below the solubility were homogenized by heating the wire in the equilibrium gas (residual) pressure for several hours at temperatures a couple hundred degrees above the solubility limit; then allowed to cool rapidly.

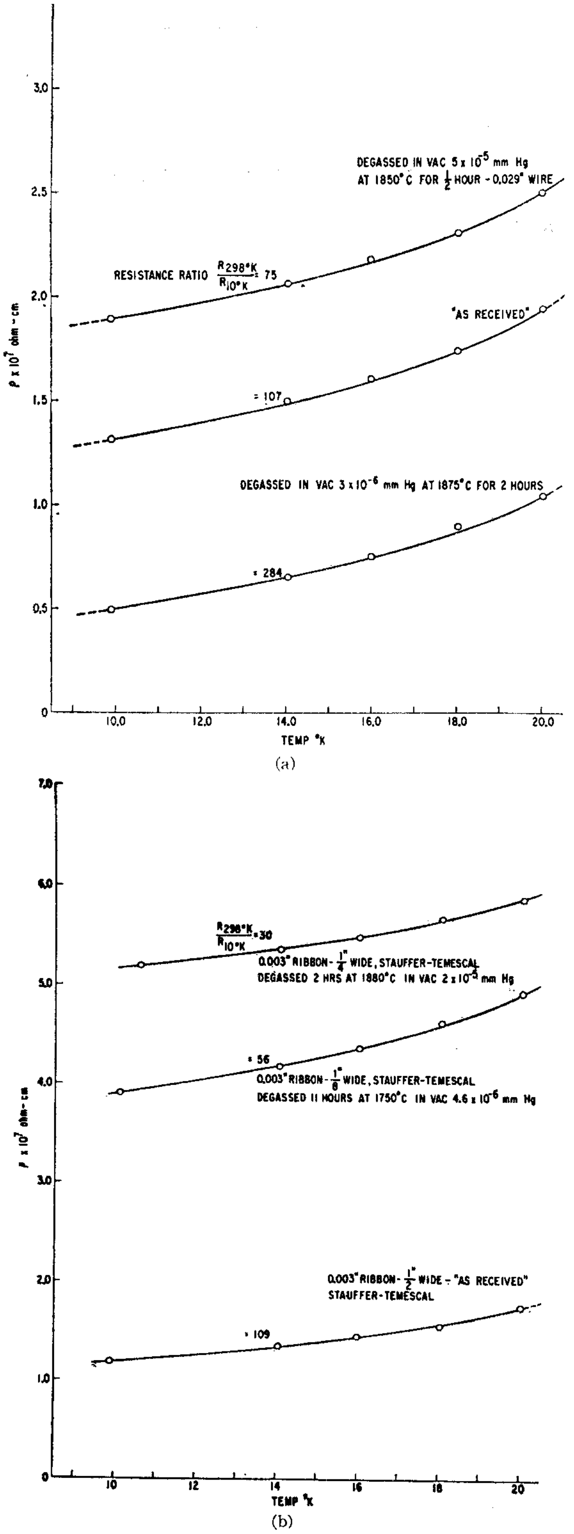
The lattice parameters of the solutions, not cited in the literature, were determined with the Debye-Scherrer technique.

The samples were prepared for microscopic observation by etching with a chemical polish consisting of 50 cc lactic acid, 30 cc HNO_3, 2 cc HF.

B. Low-Temperature Apparatus

The essential parts of the cryostat assembly that permits a temperature stable to ±0.001°K in the region 1.5–20°K, including the region 4.2–14°K, either on warming or cooling, are shown in Fig. 2. The sample holder is surrounded by copper block well insulated from the helium bath by a supporting stainless steel tube. The samples, the carbon resistor ($\frac{1}{10}$ W Allen-Bradley), and the thermocouple junction (Au-Co versus Ag-Au) are all in good thermal contact with the holder, bathing in helium-exchange gas. A second carbon resistor and thermocouple are located in the copper block. A copper shell provides housing for the high vacuum. Liquid helium surrounding the assembly is maintained at a constant pressure slightly under 1 atm (~700 mm of Hg). Temperatures may be increased or decreased conveniently by (a) controlling the energy generated by noninductively wire-wound heaters located on the copper block, and/or (b) mechanically adjusting variable-heat leak paths.

Temperatures were determined by calibrating both the carbon resistors and the thermocouples in the liquid hydrogen and liquid helium temperature regions by a procedure outlined earlier.[13] The vapor pressure versus temperature data for liquid helium is based on the E_{58} table[14]; while for liquid hydrogen (equilibrium), it is based on the Woolley, Scott, and Brickwedde[15] table. On an absolute scale the temperatures in the region 4.2 to 14°K may be accurate to better than



(a)

(b)

FIG. 1. (a) The influence of residual gas pressure, during the outgassing and annealing treatment of niobium wire (0.029-in. diam), on the low-temperature resistivity. (b) The low-temperature resistivity of some thin niobium ribbons showing the influence of temperature and residual pressure during the outgassing and annealing treatment.

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[11] A. U. Seybolt, Trans. AIME **200**, 774 (1954).

[12] Choh-Yi Ang and C. A. Wert, Trans. AIME **197**, 1032 (1956); see also J. Cost and C. A. Wert, T & AM Report No. 205, University of Illinois, 1961 (unpublished).

[13] W. DeSorbo and G. E. Nichols, J. Phys. Chem. Solids **6**, 352 (1958).

[14] F. G. Brickwedde, J. van Dijk, M. Durieux, J. R. Clement, and J. K. Logan, J. Res. Natl. Bur. Std. **A64**, 1 (1960).

[15] H. W. Woolley, R. B. Scott, and F. G. Brickwedde, J. Res. Natl. Bur. Std. **41**, 379 (1948).

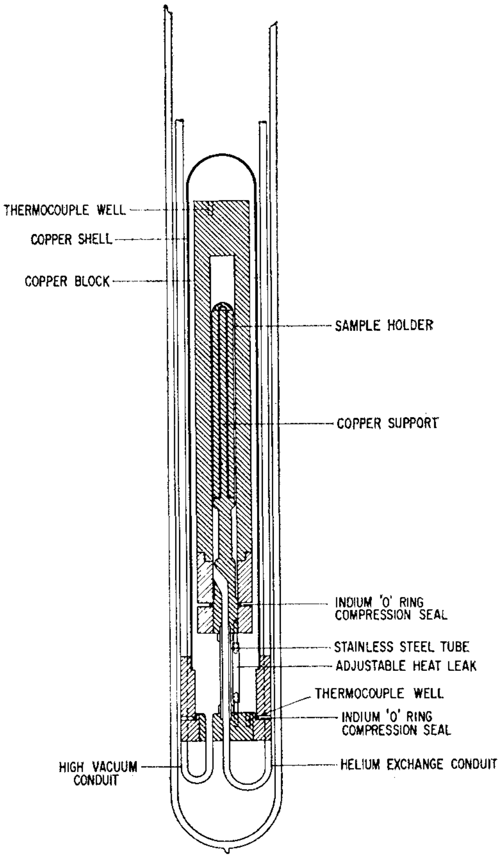

FIG. 2. A cryostat assembly for maintaining temperatures reproducible to ±0.001°K in the region 1.5–20°K, including the region 4.2–14°K.

±0.2°K, while on a relative and comparative scale they are better than ±0.05°K. In the liquid-helium region the temperature is known to better than 50 mdeg.

The longitudinal magnetic field used in the resistivity (low-current density) experiments was provided by a copper-wire wound solenoid externally cooled in liquid nitrogen. It was calibrated to an accuracy of ±1 Oe.

The critical-current and magnetic-induction measurements were carried out in the same manner described earlier.[16] The magnetic-field measurements in these two experiments were each accurate to ±10 Oe; while $-4\pi M$ values were accurate to ±5 Oe. The decision level used to determine the current carrying capacity, potentiometrically, was about 0.1 μV.

III. EXPERIMENTAL RESULTS

A. Critical Temperature

The influence of purity, strain, and solute concentrations of oxygen, nitrogen, hydrogen, and deuterium on the resistive critical temperature of niobium, at a

TABLE I. Concentrations, critical temperatures, resistivities, and magnetic properties of some interstitial solid solutions of niobium.

Solution	at.%	T_c (°K)*	ρ_n(Ω-cm) (10°K)	H_{cA} (Oe)	$\left(\frac{\partial H_{cA}}{\partial T}\right)_{T=T_c}$	γ (cal/mole deg²)×10⁴			H_N (Oe)	H_{FP} (Oe)
						$\frac{V\dagger}{8\pi}\left(\frac{\partial H_{cA}}{\partial T}\right)^2_{T_c}$	$0.17(H_0^2/T_c^2)$	Calorimetric		
Nb	...	9.46	3.5×10^{-8}	1540 (4.20°K) 1625 (3.56°K) 1730 (3.07°K)	−403	16.4±2	18.0±2	18.0±1 (32) 18.0±0.4 (33)	2700 (4.20°K) 2960 (3.50°K) 3300 (3.07°K)	1320 (4.20°K) 1390 (3.50°K) 1480 (3.07°K)
Nb+0.035 wt.% N	0.23	9.20	1.7×10^{-6}	1480 (4.20°K)	−403	...	...		5000 (4.20°K)	780 (4.20°K)
Nb+0.124 wt.% O	0.70	8.78	3.9×10^{-6}	1360 (4.20°K) 1425 (3.85°K)	−403	16.7	17.6	...	7000 (4.20°K) ~7550 (3.85°K)	580 (4.20°K) 590 (3.85°K)
Nb+0.27 wt.% O	1.52	8.04	8.2×10^{-6}	1125 (4.20°K) 1260 (3.57°K)	−403	16.8	16.4	...	~9670 (4.20°K) ~11 600 (3.57°K)	350 (4.20°K) 380 (3.57°K)
Nb+0.32 wt.% O	1.80	7.80	9.6×10^{-6}	1048 (4.20°K) 1210 (3.40°K)	−403	16.9	16.4	...	~10 300 (4.20°K) ~12 600 (3.40°K)	290 (4.20°K) 315 (3.40°K)
Nb+0.46 wt.% O	2.60	7.04	13.7×10^{-6}	840 (4.20°K) 1070 (3.10°K)	−403	17.0	16.0	...	~11 550 (4.20°K) ~15 000 (3.10°K)	170 (4.20°K) 200 (3.10°K)

* Resistive transition.
† The molar volume, V, of these interstitial Nb-O solid solutions is from data of R. W. Powers. The author is grateful to him for permission to use these values prior to publication.

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[16] C. P. Bean, Margaret V. Doyle, and A. G. Pincus, Phys. Rev. Letters 9, 448 (1962).

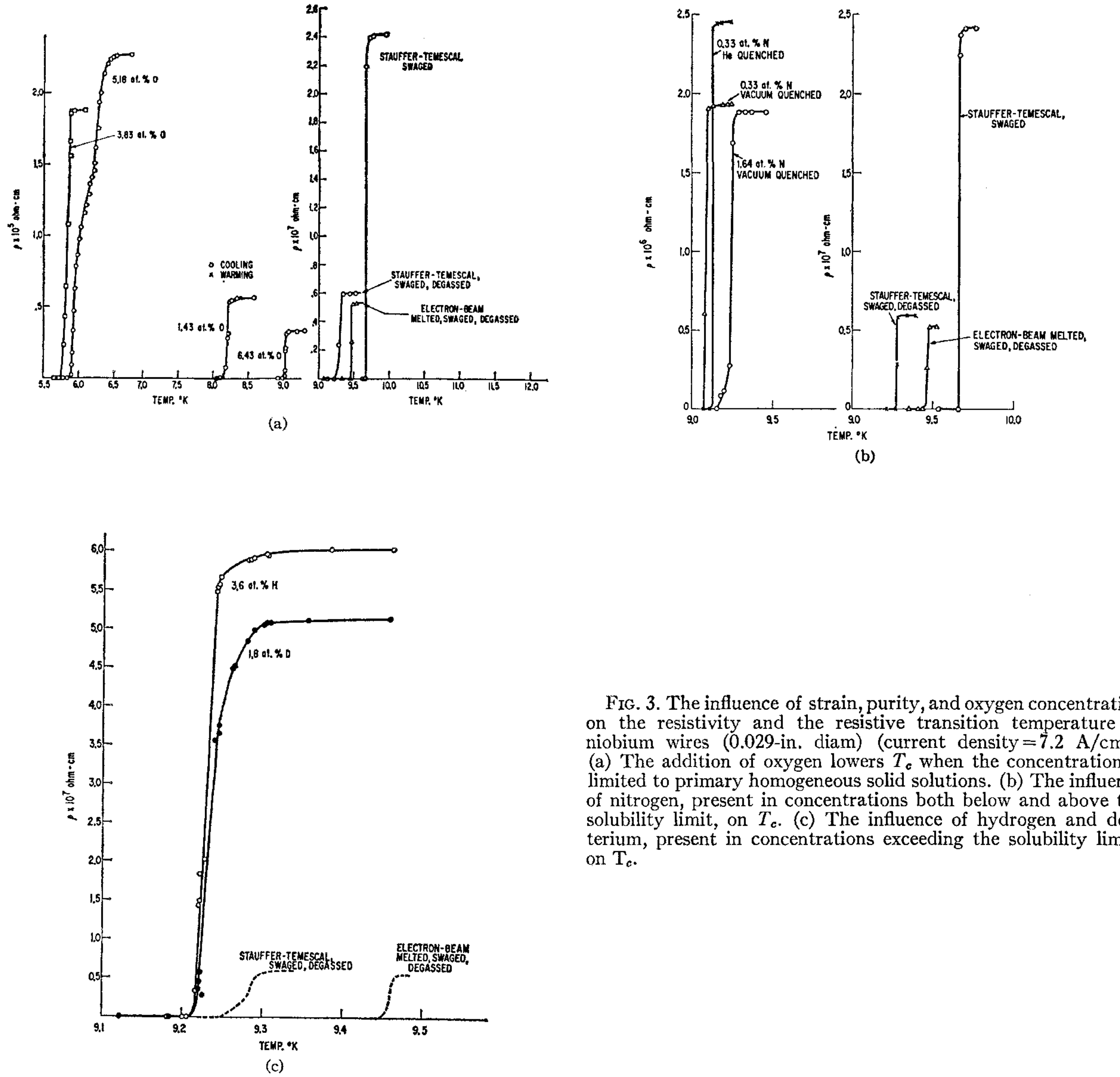

FIG. 3. The influence of strain, purity, and oxygen concentration on the resistivity and the resistive transition temperature of niobium wires (0.029-in. diam) (current density = 7.2 A/cm^2). (a) The addition of oxygen lowers T_c when the concentration is limited to primary homogeneous solid solutions. (b) The influence of nitrogen, present in concentrations both below and above the solubility limit, on T_c. (c) The influence of hydrogen and deuterium, present in concentrations exceeding the solubility limit, on T_c.

current density of 7.2 A/cm^2, is presented in Figs. 3(a), 3(b), and 3(c), respectively. The resistive critical temperature is here defined in the usual manner, namely, the temperature at which the resistance R has attained one half the normal value, R_n, at the top of the transition.

A wire of niobium cold-worked by swaging and drawing to 0.020-in. diam has a transition temperature equal to 9.6$_7$°K ($R_{298\,°\mathrm{K}}/R_{10\,°\mathrm{K}}=68$). This critical temperature is comparable to that reported by Minnigerode[17] for cold-worked niobium. The critical temperature decreases to 9.2$_0$°K after the wire is outgassed and annealed ($R_{298\,°\mathrm{K}}/R_{10\,°\mathrm{K}}=280$). A 0.030-in. diam wire drawn from the ingot, electron-beam melted five passes, followed by the outgassing and annealing treatment ($R_{298\,°\mathrm{K}}/R_{10\,°\mathrm{K}}\approx 500$), has a transition temperature equal to 9.4$_6$°K in good agreement with the results of both Minnigerode[17] and Calverley.[18] (For critical temperature of niobium reported by various investigators using different methods, see Ref. 19. For a strict comparison the impurities listed should be considered.)

Oxygen, added interstitially to niobium, and kept at a concentration below the solubility limit, depresses the

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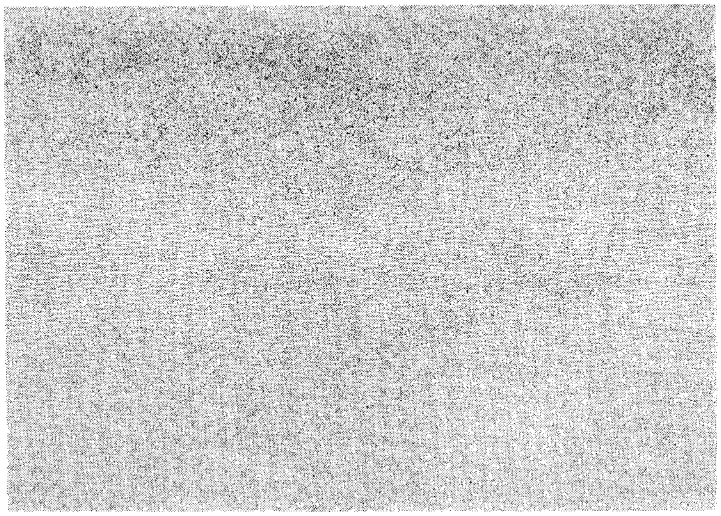
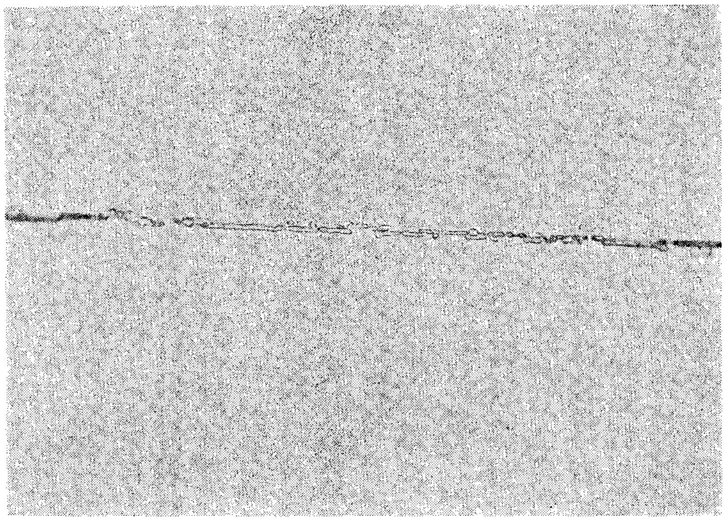
[17] C. von Minnigerode, Z. Physik 154, 442 (1959).

[18] A. Calverley (private communication).

[19] B. W. Roberts, Progr. Cryog. 4 (1963) (to be published).



(a)



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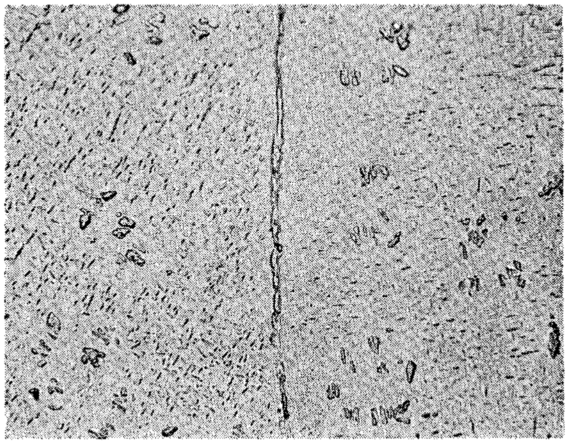

(c)

FIG. 4. Photomicrographs of niobium wires (0.029-in. diam). (a) Containing 5.18 at.% oxygen. Mag. 500×. No visible structure except in the grain boundary. Slow cooled (quenched in vacuum). (b) Containing 5.65 at.% oxygen. Mag. 500×. Possibly NbO in grain boundary (slow cooled). (c) Containing an apparent amount of 6.43 at.% oxygen. The small needle-like structure is probably a nitride, "Nb_2N," due to nitrogen contaminant. The other structure may be NbO. Mag. 1000×. (Slow cooled.)

transition temperature (see Table I). At an oxygen concentration equal to 3.83 at.%, $T_c=5.8_4$°K. This concentration of oxygen represents, approximately, the solubility limit at 1000°C (see Fig. 6, Ref. 11) the temperature from which the specimen was quenched. Increasing the oxygen concentration beyond this value raises T_c from the minimum value. When 6.43 at.% oxygen has been introduced in the lattice, T_c reaches a value equal to 9.0_2°K. When the solubility has been exceeded, oxygen precipitates yielding various oxides.[20–23] Optical micrographs of three niobium speci-

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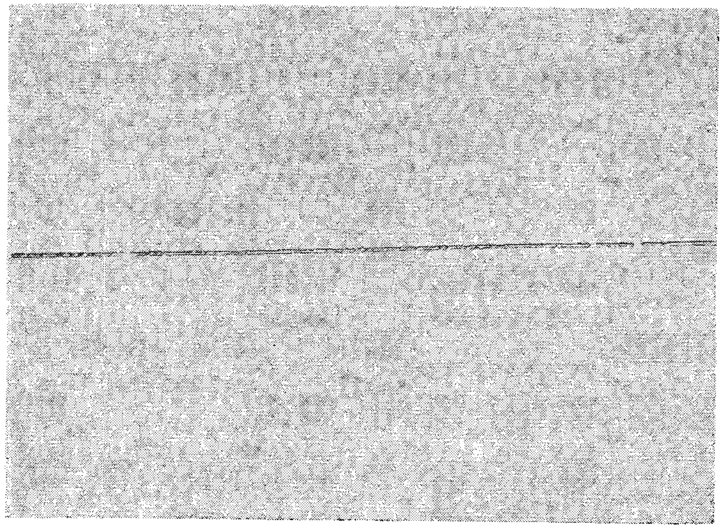
[20] N. Norman, in International Union Crystallography Fifth International Congress and Symposia, Cambridge, England, 1960 (unpublished), abstract in Acta Cryst. **13**, 1013 (1960).

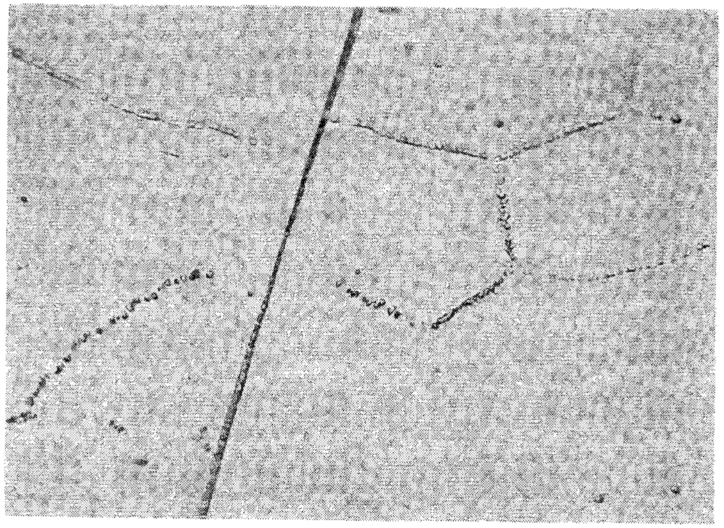
[21] G. L. Miller, *Tantalum and Niobium* (Butterworths Scientific Publications Ltd., London, 1959).

[22] N. Norman, J. Less-Common Metals **4**, 52 (1962).

[23] N. Norman, P. Kotstad, and O. J. Krudtao, J. Less-Common Metals **4**, 124 (1962).



(a)



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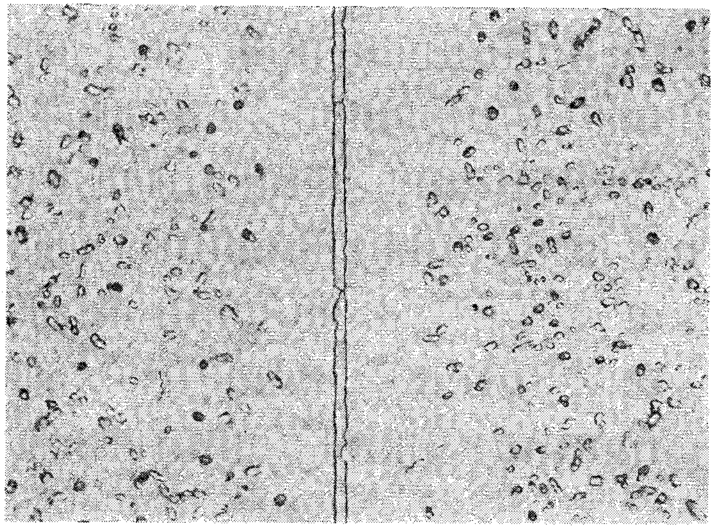
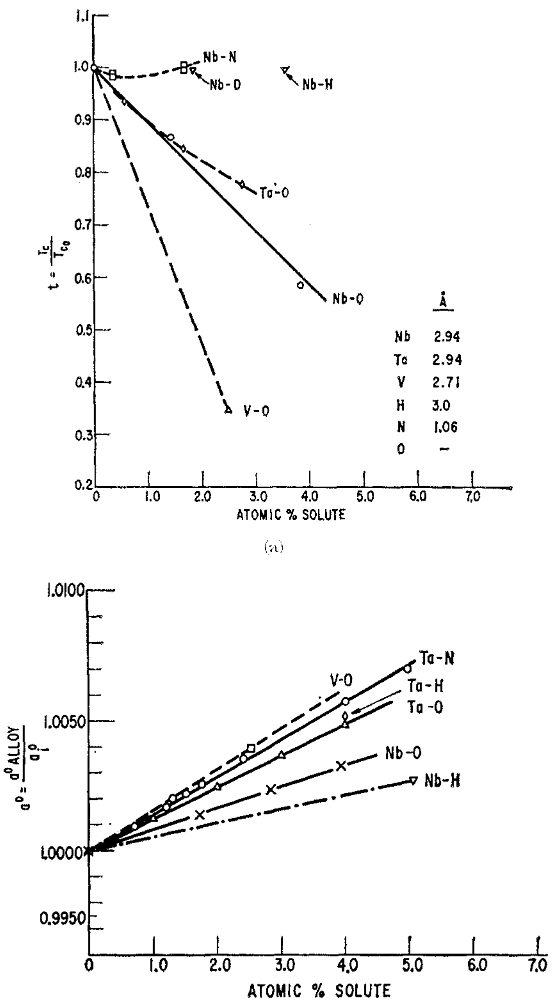


(c)

FIG. 5. Photomicrographs of niobium wires (0.029-in. diam). (a) Containing 0.33 at.% nitrogen cooled in helium exchange gas. This concentration is close to the solubility limit. Discontinuous structure at grain boundary is probably "Nb_2N." (b) Containing 0.33 at.% nitrogen slow cooled (vacuum quenched). Note the tendency for the solute atom to concentrate at lattice irregularities such as low-angle and regular high-angle grain boundaries. Mag. 1000×. (c) Containing 1.64 at.% nitrogen (above the solubility limit) (slow cooled). Note the grain boundary is lined with nitride, probably "Nb_2N," and that the nitride is also within the grain with an apparent depletion near the grain boundary. Mag. 1000×.



(a)

(b)

Fig. 6. The effect of concentration of some interstitial solute atoms on (a) the critical temperature of niobium, vanadium and tantalum, where t is the reduced temperature; T_c the critical temperature of the solution; and T_{c_0}, the critical temperature of pure base metal. (b) The reduced lattice parameter of some solid solutions of Nb, V, and Ta (see Ref. 27). a_0 is the lattice parameter of the solution, a_{i_0} is the lattice parameter of the pure solvent.

mens with oxygen concentration above the solubility limit are presented in Figs. 4(a), 4(b), and 4(c).[24]

Nitrogen present in niobium in amounts equal to 0.33 at.% depresses the transition temperature to 9.1_2°K [Fig. 3(b)], representing a slight decrease from that of the pure material. This concentration represents the solubility limit of nitrogen in niobium quenched from 1200°C,[12] being smaller than that of oxygen in niobium. Increasing the cooling rate [e.g., cooling the specimen in helium exchange gas instead of in vacuum, after introducing the gas at elevated temperature, compare Figs. 5(a) and 5(b)] results in only a slight change in critical temperature. At a nitrogen concentration exceeding the solubility limit as in Nb+1.64 at.% N [see Fig. 5(c)], T_c rises to a value 9.2_4°K.

The presence of hydrogen (or deuterium) in amounts small but in excess of the solubility limit[25] results in only slight changes in T_c. In Fig. 3(c), for specimen, Nb+3.6 at.% H, T_c is 9.2_2°K; while for Nb+1.8 at.% D it is equal to 9.2_3°K.

The influence of concentration of interstitial on the critical temperature of niobium, reported here, is summarized in Fig. 6(a). For Nb-O solutions, the transition temperature is decreased approximately linearly, 0.93°K/at.%. Oxygen present in tantalum[1] or in vanadium[26] at concentrations below the solubility limit also lowers T_c for each of these transition metals.

The reduced lattice parameter a^0 as a function of concentration of Nb, V, and Ta containing interstitial solutes (see Ref. 27) are presented in Fig. 6(b). A linear relationship is evident between a^0 and at.% solute.

B. Resistivity in the Normal State

The resistivity, ρ_n, in the normal state for niobium strained, outgassed, and annealed, and niobium containing various solute concentrations, may also be obtained by examining Figs. 3(a), 3(b), and 3(c). ρ_n for cold-worked niobium wire (0.020-in. diam) is equal to 2.4×10^{-7} Ω-cm. Upon outgassing and annealing this specimen, the resitivity decreases to approximately 0.6×10^{-7} Ω-cm. Resistivity values somewhat below this latter value have been obtained (see Table I) on niobium wire (0.030-in. diam) electron-beam melted five passes.

The addition of interstitial oxygen decreases the resistivity 5.2 μ Ω-cm/at.% (Table I). At the solubility limit, Nb+3.83 at.% O, ρ_n is equal to 1.9×10^{-5} Ω-cm. As the concentration of oxygen exceeds the solubility limit, there is an apparent continued rise in ρ_n followed by a decrease in value at the higher concentrations. For niobium containing 5.18 at.% O, the resistivity is equal to 2.3×10^{-5} Ω-cm; but niobium containing 6.43 at.% O has a resistivity equal to 3.4×10^{-6} Ω-cm.

Nitrogen present interstitially in the niobium lattice also enhances the resistivity. In Nb+0.33 at.% N (the solubility limit), ρ_n is 1.9×10^{-6} Ω-cm for a specimen cooled in vacuum after introducing the solute at 1200°C. For somewhat more rapid cooling, this increases to approximately 2.4×10^{-6} Ω-cm. A sample containing 1.64 at.% N, a concentration in excess of the solubility limit and vacuum quenched, ρ_n has a value equal to 1.8×10^{-6}

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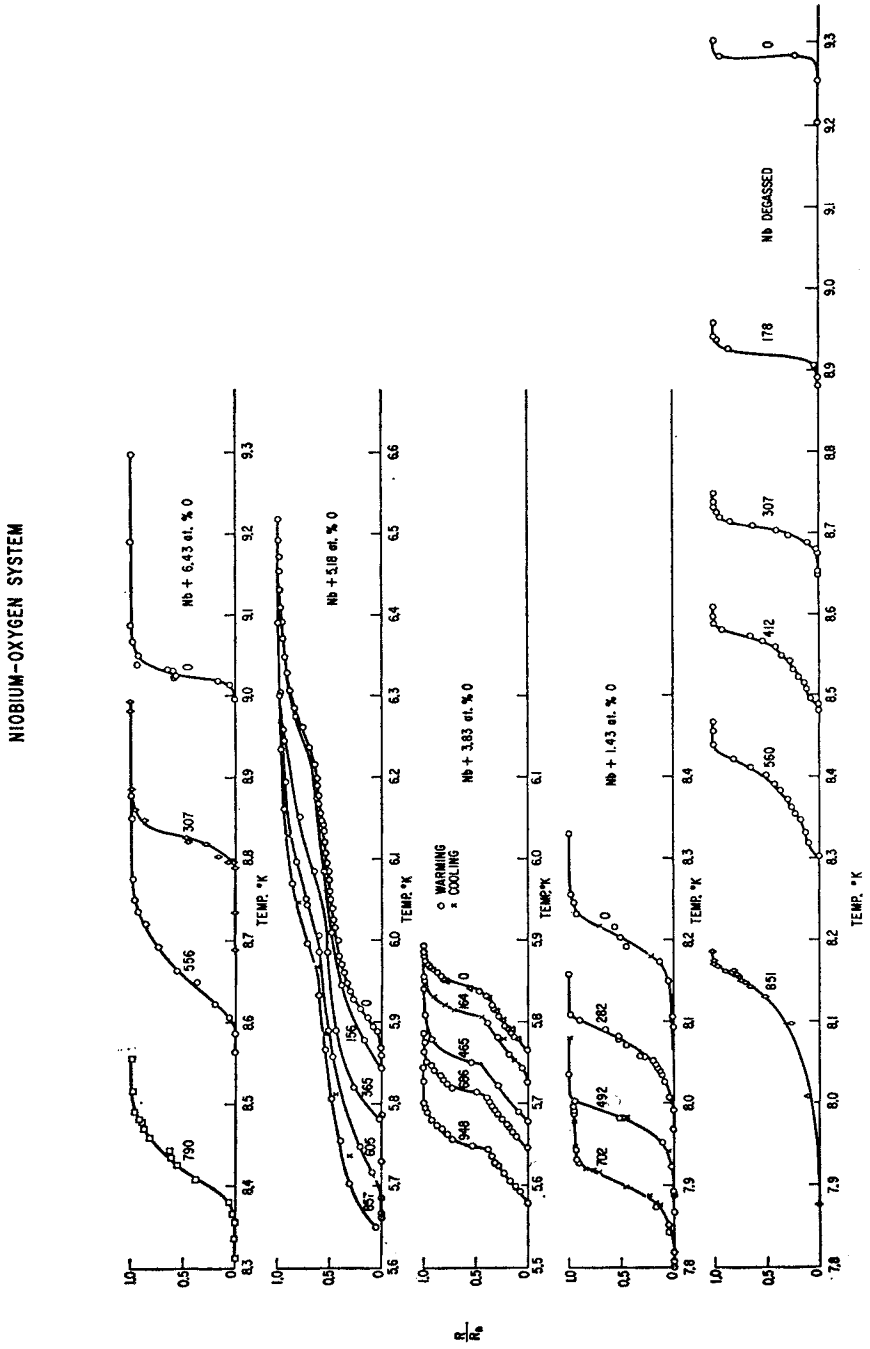
[24] In addition to the presence of the oxide, there may also be some nitride, probably "Nb_2N", due to some nitrogen contaminant in the oxygen gas. This nitride [see also Figs. 5(a), 5(b), and 5(c)] is generally recognized in the literature but does have an homogeneity range of a few percent.

[25] W. M. Albrecht, W. D. Goode, and M. W. Mallet, J. Electrochem. Soc. **106**, (11), 981 (1959).

[26] W. DeSorbo and G. E. Nichols (unpublished results).

[27] Nb-O, Ref. 11; Ta-H, Nb-H, Ref. 3; Nb-H, W. F. Sheely, J. Less-Common Metals **2**, 399 (1960); TaN, Ta-O, J. J. English, BMIC Report 152, 1961, Battelle Memorial Institute, Columbus 1, Ohio, pp. 66 and 68 (unpublished).



NIOBIUM-OXYGEN SYSTEM

(a)

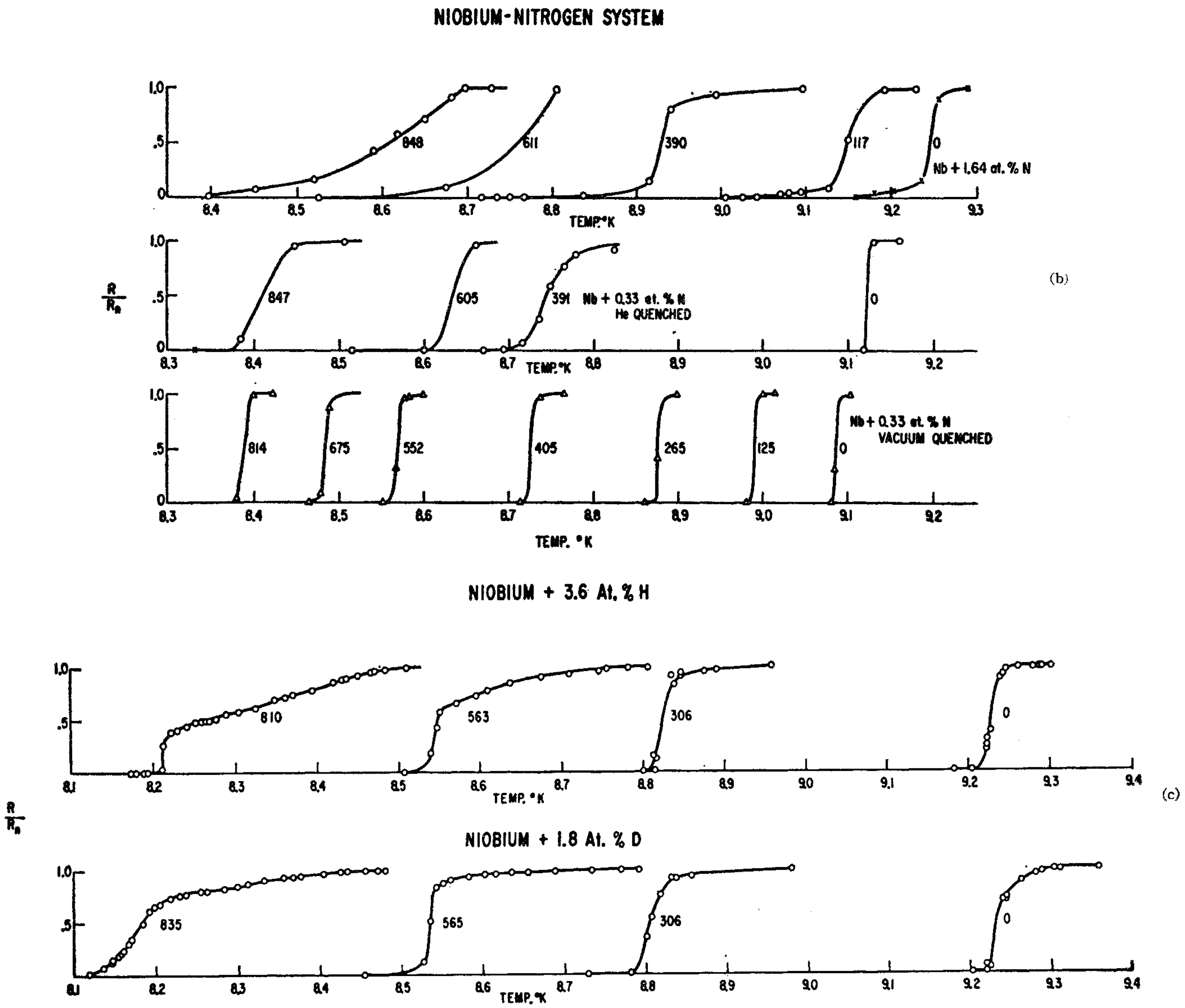
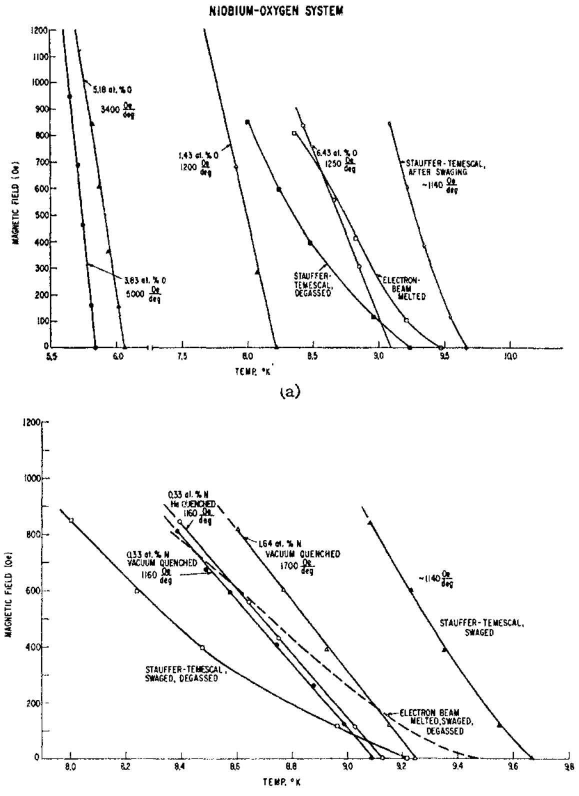


Fig. 7. Resistive transition characteristics, in a longitudinal magnetic field, of niobium wires (0.029-in. diam) containing various amounts of dissolved gases: (a) oxygen; (b) nitrogen; (c) 3.6 at.% hydrogen and 1.8 at.% deuterium. (Current density=7.2 A/cm^2.) Numbers near each transition curve refer to the field (Oe).



(a)

(b)

FIG. 8. The initial slope of the critical magnetic field versus temperature, $(\partial H_{cR}/\partial T)_{T\rightarrow T_c}$, deduced from resistive transition data at $R/R_n = 0.5$ for some niobium containing (a) oxygen and (b) nitrogen. (Current density = 7.2 A/cm².)

Ω-cm. This represents little or no change with the similarly heat treated niobium containing the smaller nominal nitrogen concentration [Fig. 3(b)].

Hydrogen or deuterium present in amounts small but in excess of the solubility limit also increase resistivity but to a smaller extent. ρ_n equals 6.0×10^{-7} Ω-cm for Nb+3.6 at.% H and 5.1×10^{-7} Ω-cm for Nb+1.8 at.% D.

C. Resistive Transition in Longitudinal Fields

Some superconducting transitions, examined resistively in longitudinal magnetic fields at low current density (J = 7.2 A/cm²), are illustrated for (a) Nb and Nb-O, (b) Nb-N, and (c) Nb-H and Nb-D, solutions in Figs. 7(a), 7(b), and 7(c), respectively.

For outgassed and annealed niobium, the transition in zero field is relatively steep, but tends to spread out with increasing field. For the Nb-O solutions, when the concentration of oxygen is in the vicinity of the solubility limit (Nb+3.83 at.% O), large temperature variations in the transition become apparent. The behavior becomes even more pronounced above this limit (e.g., Nb+5.18 at.%). At higher concentrations of oxygen, such as Nb+6.43 at.% O, the curves begin to resemble those observed on the outgassed niobium. Another interesting feature of the resistive transition behavior in these solutions at constant field is the dependence of temperature of the transition on the magnetic field. As the concentration of oxygen increases in the interstitial region below the solubility limit, the shift of the transition to lower temperatures per unit field becomes smaller; while above the solubility limit this shift to lower temperature begins to increase again with field. This behavior is more clearly illustrated in Fig. 8(a) where the field, H_{cR}, is plotted against temperature. H_{cR} is defined in the usual manner, namely, that field which at a given temperature restores the resistance to half the normal value ($R/R_n = 0.5$). For "as-received" niobium wire (unannealed), the initial slope of the critical magnetic field versus temperature, $(\partial H_{cR}/\partial T)_{T\rightarrow T_c} = -1140$ Oe/deg; while for the same niobium outgassed and annealed, $(\partial H_{cR}/\partial T)_{T\rightarrow T_c}$ is -530 Oe/deg. However, the addition of oxygen interstitially to niobium, previously annealed and outgassed, actually increases this slope. The maximum value of -5000 Oe/deg is achieved for specimen, Nb+3.83 at.% oxygen, the nominal solubility limit. When the concentration of oxygen increases beyond this, $(\partial H_{cR}/\partial T)_{T\rightarrow T_c}$ decreases. For specimen, Nb+6.43 at.%, it has a value of -1250 Oe/deg—only slightly above that of the original "as-received" niobium.

For niobium containing nitrogen in concentrations near the solubility limit (Nb+0.33 at.% N) a steeper transition is observed [Fig. 7(b)] when the specimen is cooled at a slower rate (in vacuum) than if cooled more rapidly in helium exchange gas. When the nitrogen is present in amounts exceeding the solubility limit (e.g., Nb+1.64 at.% N) the resistivity at the base of the transition curve decreases gradually to zero over a wide temperature range. H_{cR} versus temperature for these three specimens is shown in Fig. 8(b). $(\partial H_{cR}/\partial T)_{T\rightarrow T_c}$ values for two specimens of Nb+0.33 at.%, cooled at different rates, are identical, namely, -1160 Oe/deg. For niobium containing 1.64 at.% N, $(\partial H_{cR}/\partial T)_{T\rightarrow T_c}$ has increased to -1700 Oe/deg.

For samples Nb+3.6 at.% H or Nb+1.8 at.% D [Fig. 7(c)] the top of the transition broadens at the higher fields in a manner qualitatively different from that observed in Nb-O or Nb-N solutions of comparable concentration. The curves are similar to those observed in tantalum inhomogeneously strained[1] where the sharp onset of the resistance was coincident with almost total flux penetration.

D. Magnetization and Hysteresis

The magnetic behavior of (a) niobium, both before and after outgassing and annealing, and (b) niobium containing oxygen or nitrogen in amounts both below and above the solubility limit are presented in Figs. 9 and 10. M is the magnetization per unit volume, H the applied field.

The magnetization peak and the hysteresis loop are smaller in outgassed and annealed niobium when compared to the material in the "as-received" state. Both of these magnetic characteristics decrease as the con-

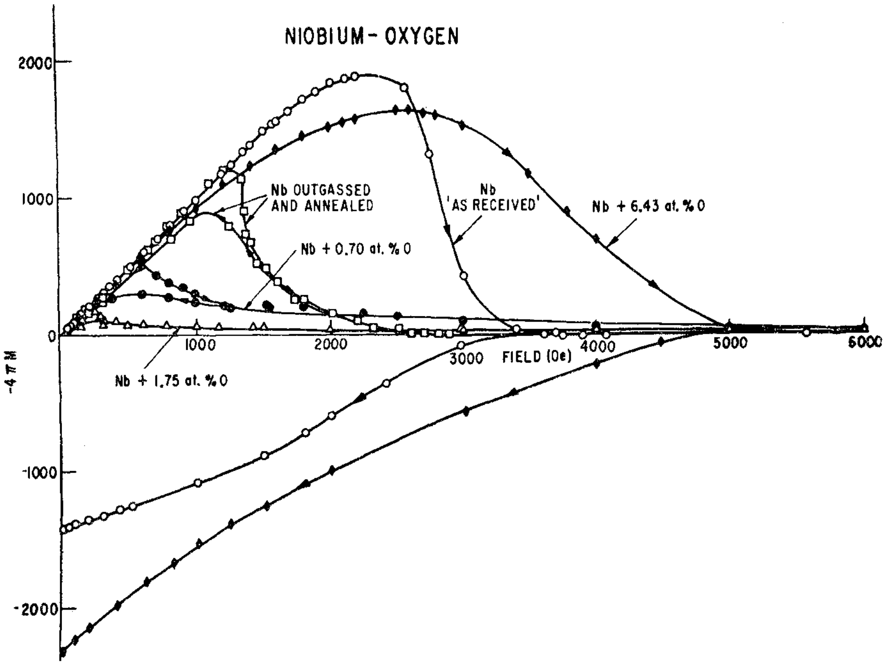


FIG. 9. The magnetization of niobium (a) "as-received" ($R_{298°K}/R_{10°K}=68$), and (b) electron-beam melted, outgassed and annealed ($R_{298°K}/R_{10°K}\approx 500$), (c) niobium solutions containing oxygen both below and above the solubility limit (Temperature = 4.2°K).

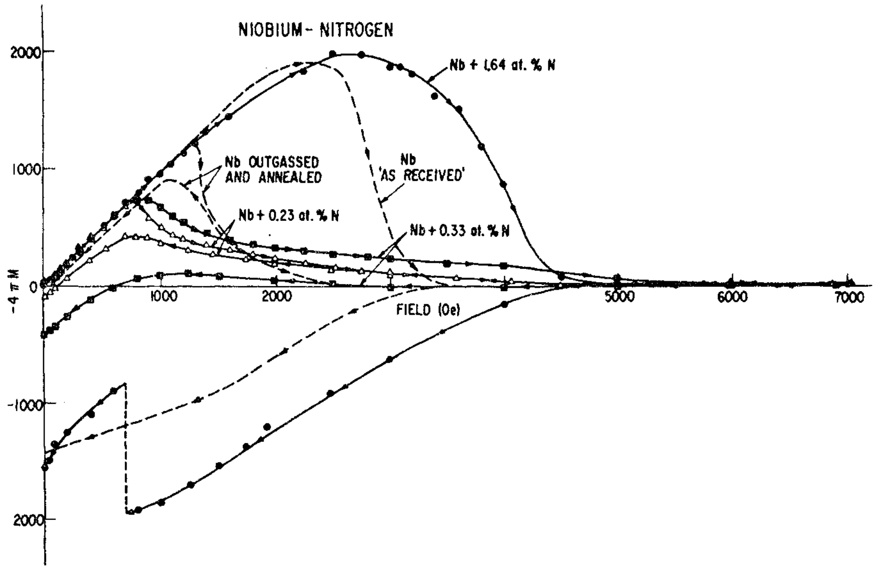


FIG. 10. The magnetic behavior of niobium containing nitrogen both below and above the solubility limit (Temperature = 4.2°K) compared to niobium "as-received" and niobium outgassed and annealed.

centration of the interstitial is increased but remaining below the solubility limit. Coincident with the appearance of the magnetization peak at lower applied fields is the larger field required to decrease $-4\pi M$ to zero. Niobium, in the "as-received" state (strained) and the metal, previously annealed and outgassed but to which oxygen or nitrogen has been added in amounts exceeding the solubility limit, exhibit large magnetization peaks and large hysteresis loops.

E. Critical Current in Transverse Field

The critical current, I_c, obtained on some 0.030-in.-diam wire specimens are shown in Fig. 11. Niobium "as-received" or unannealed is a better current carrier than similar niobium after undergoing the outgassing and annealing treatment. With oxygen present in interstitial amounts, at or below the solubility limit, I_c is small even at zero field. As H increases from zero, I_c drops rapidly. However, when the solubility limit of oxygen has been exceeded, the specimen appears to carry more current at higher fields.

IV. DISCUSSION OF RESULTS

A. T_c, ρ_n and the Interstitial Solute

As mentioned above, the addition of interstitial oxygen to niobium decreases T_c, 0.93°K/at.%; while the resistivity is increased 5.2 μΩ-cm/at.%. This latter value is similar to that reported by Seraphim *et al.*[1] on

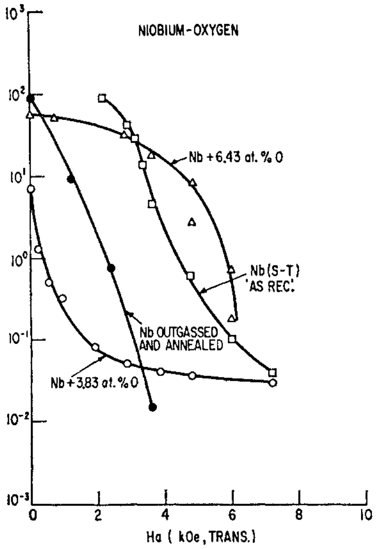


FIG. 11. The current-carrying capacity in transverse magnetic field for niobium wires (0.029-in. diam) (a) "as-received," (b) outgassed and annealed, (c) containing 3.83 at.% oxygen, and (d) containing 6.43 at.% oxygen. ($T=4.2$°K.)

the influence of dilute concentrations of interstitial nitrogen on the resistivity of tantalum (i.e., 5.1 $\mu\Omega$-cm/at.%). The resistivity change per at.% brought about by interstitial solutes added to niobium or to tantalum is larger than that brought about by similar additions of metallic solutes of column IVA or VIA of the periodic table (see e.g., Fig. 9, Ref. 5). Another point of difference between substitutional (metals, group IVA and VIA) and interstitial (nonmetallic) additions to the transition metal is the correlation between T_c and lattice parameter, a. T_c usually *increases* with *increasing* a; or *decreases* with *decreasing* a when one of these metallic solutes is added to the transition metal.[5] In interstitial solutions, the *decrease* in T_c with concentration [Fig. 6(a)] is accompanied by an *increase* in lattice parameter a [Fig. 6(b)]. Correlations between T_c (decrease) and a (increase) have been reported earlier by Horn[3] involving larger concentrations of hydrogen and nitrogen in both tantalum and niobium.

Increasing the cooling rate of a specimen upon introduction of the interstitial solute results in an additional increase in ρ_n [Fig. 3(b)]. This change may be due to the stabilization of the point defects by the solute atom. T_c, however, remains virtually unaffected.[28] In addition to this, a high cooling rate prevents precipitation on cooling; whereas a lower cooling rate assists cluster or precipitate formation [compare Figs. 5(a) and 5(b)].

The increase in T_c and the decrease in ρ_n evident in the NbO system when the oxygen concentration exceeds (approximately) the solubility limit [Fig. 3(a)] implies a possible depletion of some of the interstitial oxygen when precipitation occurs. That is, precipitation at the temperature of introduction of oxygen apparently leads to further precipitation of dissolved oxygen on cooling. In addition, some of the substitutional impurities present in niobium may form oxides, some of which may be volatile. The oxides of niobium and of metallic impurities interspersed in the matrix and at lattice irregularities, such as dislocations, may contribute to lattice strains to help increase T_c.[29]

B. Comparison of Magnetic Data with Negative Surface Energy Superconductors

The magnetization curves obtained on niobium containing oxygen or nitrogen in interstitial concentration below the nominal solubility limit (Figs. 9 and 10) approach the magnetic behavior predicted by negative surface energy models.[6,7] This interpretation has already been suggested for pure niobium.[30] The theoretical magnetization curves described by Abrikosov and Goodman[6,7] are characterized by the penetration of the applied field at a value, H_{FP}, smaller than the thermodynamic critical field H_c (Fig. 12). At a field $H_N > H_c$, the material supposedly is completely normal. The treatment assumes a defect-free homogeneous material and the predicted magnetization behavior is reversible. Arguments have been advanced in these treatments to show that both H_{FP} and H_N depend on H_c, ρ_n, and γ, the coefficient of the electronic specific heat. Assuming that the ascending magnetization curves for the homogeneous interstitial solid solutions are a close approximation to the magnetic behavior of negative surface energy superconductor, the value of H_N and H_{FP} have been evaluated from these curves and are listed in Table I.

According to Goodman,[7] the Abrikosov theory leads to the following relationship

$$H_N/H_c=\sqrt{2}\kappa_0+0.0106\gamma^{1/2}\rho \tag{1}$$

valid for $H_N > H_c$, where γ is in ergs/cm^3 deg^2, ρ_n is in $\mu\Omega$-cm, and κ_0 a constant reflecting the balance of surface energy terms for a pure material with an infinite mean-free path. For some materials, the electronic structure may be such that κ_0 is greater than $1/\sqrt{2}$.[30,31]

It is of interest to compare Eq. (1) with the magnetization and resistivity data obtained here on the interstitial solid solutions of niobium (Fig. 13, Table I). H_c is approximated from the area under the magnetization curve considering the ascending field and ignoring the relatively small irreversibility occurring at the lower fields.[30,32] It is referred to as H_{cA}. The ratio, H_N/H_{cA}, plotted as a function of resistivity, ρ_n, is described quite well by the linear relationship considering the approximation used in evaluating H_c. The straight line in

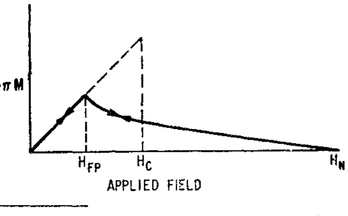


FIG. 12. The magnetic behavior predicted for a "negative surface energy" superconductor (Ref. 7).

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[28] W. DeSorbo, J. Phys. Chem. Solids **15**, 7 (1960).

[29] D. Schoenberg, *Superconductivity* (Cambridge University Press, New York, 1960), 2nd ed., pp. 10 and 73–77.

[30] T. F. Stromberg and C. A. Swenson, Phys. Rev. Letters **9**, 370 (1962).

[31] B. B. Goodman, Phys. Letters **1**, 215 (1962).

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

Fig. 13 has been calculated from the parameters,[33,34] $\gamma = 6993$ ergs/cm^3 deg^2, $H_N/H_{cA} = 1.75$, and $\rho_n = 3.5\times 10^{-8}$ Ω-cm evaluated experimentally for pure niobium. Similar correlations have been shown earlier for some well-prepared Pb-base alloys.[32]

Considering the difference in resistance ratio of the two niobium specimens, the value of H_N/H_c compares favorably with the value 1.65 reported earlier.[30] The temperature dependence of $h_2 = H_N/H_{cA}$ and $h_1 = H_{FP}/H_{cA}$ for purified niobium used in this work is also in good agreement with the previous result.[30]

The large hysteresis loop in the magnetization curve observed for niobium "as received" (strained) and for niobium containing the interstitial solute in concentrations above the solubility limit obscures the negative surface energy behavior.[35,36] In these alloys the resistivity, ρ_n, or the mean free path, may not be altered much by strain or by cold work[32,37] and H_N which depends on ρ_n [Eq. (1)] would not be expected to change very much. H_N observed on niobium annealed (unstrained) and "as-received" (strained) actually does show only small differences (Fig. 9). The somewhat higher value for the "as received" specimen may be due to higher initial interstitial solute concentration resulting in a higher ρ_n. The decrease in ρ_n observed [see Fig. 3(a)] when oxygen concentration exceeds the solubility limit suggests, as mentioned earlier, depletion of oxygen during the precipitation reactions. Correspondingly, a decrease in H_N would be anticipated from Eq. (1).[32,38] This is observed both for Nb+6.43 at.% O (Fig. 9) and Nb+1.64 at.% N (Fig. 10).

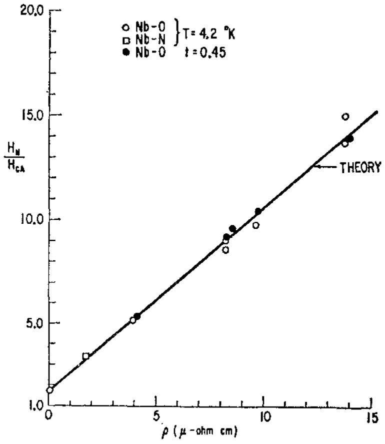

FIG. 13. The dependence of H_N/H_{cA} on the resistivity in the normal state for some Nb-O and Nb-N solutions. The solid line is based on Eq. 1 with $\gamma = 6993$ ergs/cm^3 deg^2, and $H_N/H_{cA} = 1.75$ for pure Nb.

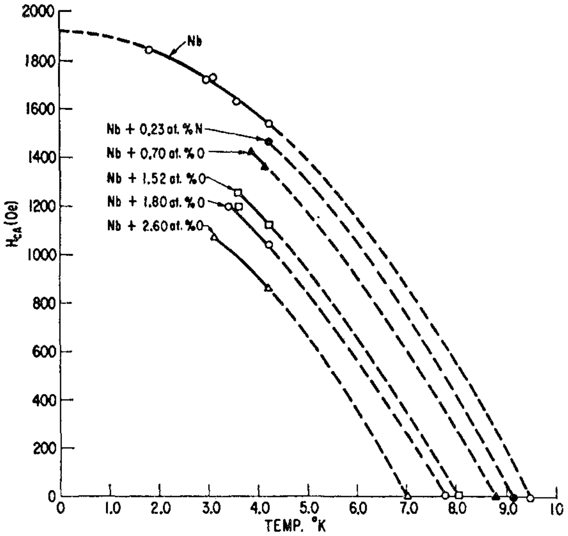

FIG. 14. The critical field as a function of temperature evaluated from the area under the ascending magnetization curve for Nb and some of its interstitial solid solutions.

C. The Constancy of γ in Interstitial Solutions

The dependence of H_N/H_{cA} on mean free path (Fig. 13) suggests that γ changes relatively little in niobium upon the addition of an interstitial atom such as oxygen. The same conclusion may be arrived at from the relationship H_{cA} versus T. In Fig. 14, T°K refers to bulk critical temperature, except for those T_c values at zero field which were obtained resistometrically at low current density (see above). It is assumed that this latter value represents a close approximation to T_c for bulk specimens.[1] The H_{cA} versus T curves for Nb and for the various interstitial solutions can be described approximately by the quadratic equation,[39]

$$H_{cA} = H_0[1-(T/T_c)^2]. \qquad (2)$$

For pure niobium, H_0 is calculated from Eq. (2) and found to be 1920±50 Oe, in good agreement with the value 1944 Oe derived from calometric data[33,34] and the values 1960±40 Oe[30] and 1980±60 Oe[40] evaluated from magnetic data. Within the precision of the measurements, the ratio H_0^2/T_c^2 (T_c in zero field), remains constant. In the BCS theory[41] this ratio is given by the relationship

$$H_0^2/T_c^2 = k\gamma, \qquad (3)$$

referred to as the similarity principle or the law of corresponding states.

The similarity may be illustrated in still another manner, namely, through the constancy of the slope $(\partial H_{cA}/\partial T)_{T\to T_c}$. If the single law given by Eq. (2) is applicable, it can be shown [see, e.g., Refs. 2 and 42] that

$$\gamma = (V/8\pi)(dH_c/dT)^2{}_{T\to T_c}, \qquad (4)$$

where $H_c \approx H_{cA}$. The values of γ, evaluated from Eqs. (3) and (4), are listed in Table I. Within experi-

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[33] C. Chou, D. White, and H. L. Johnston, Phys. Rev. **109**, 788 (1958).

[34] A. T. Hirschfeld, H. A. Leupold, and H. A. Boorse, Phys. Rev. **127**, 1501 (1962).

[35] P. S. Swartz, Phys. Rev. Letters **9**, 448 (1962).

[36] J. J. Hauser, Phys. Rev. Letters **9**, 423 (1962).

[37] T. G. Berlincourt and R. R. Hake, Phys. Rev. Letters **9**, 293 (1962).

[38] J. D. Livingston, J. Appl. Phys. 34, 3028 (1963).

[39] Reference 23, p. 9.

[40] A. Calverley, K. Mendelssohn, and R. M. Rowell, Cryogenics 2, 26 (1961).

[41] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[42] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. (London) **A160**, 127 (1937).

mental error they may be considered essentially constant. γ evaluated for niobium by either procedure is in good agreement with that derived experimentally from calorimetric data.[33,34] The initial slope of the critical magnetic field vs temperature, $(\partial H_{cA}/\partial T)_{T\rightarrow T_c}=-403$ Oe/deg, approximated for pure niobium, compares favorably with the value -415 Oe/deg reported by Chou *et al.*[33] from calorimetric measurements.

D. Some Evidence for the Presence of Defects and/or Inhomogeneities in Interstitial Solutions

Evidence may be cited from both magnetic and resistometric measurements for the existence of defects and/or inhomogeneities still present in niobium of the purity reported here as well as in Nb-O and Nb-N solutions even at small solute concentrations.

The small but finite departure from complete reversibility observed in the magnetization curves of niobium and its interstitial solutions (Figs. 9 and 10) indicate the presence of defects and inhomogeneities.[32,38,43,44]

In many cases resistance measurements especially at small measuring current are more sensitive to small traces of residual or remanent superconductivity, which may involve defects and substructure occupying only a small fraction of the total volume (e.g., see Ref. 1), than the magnetic method which measures the superconducting transition of the bulk of the material. The rate of change of the resistive critical field, H_{cR} (defined above), with temperature measured at low current density and near T_c may serve as a good criteria for defect concentration [Figs. 8(a) and 8(b)]. This may be illustrated by comparing the initial slope of the *resistive* critical magnetic field, $(\partial H_{cR}/\partial T)_{T\rightarrow T_c}$, equal to -530 Oe/deg for high-purity niobium with the value -403 Oe/deg evaluated from magnetic data (Fig. 14) or the value -415 Oe/deg obtained calorimetrically.[33] For "as-received" niobium $(\partial H_{cR}/\partial T)_{T\rightarrow T_c}$ equals -1140 Oe/deg. However, the addition of oxygen, supposedly interstitially, to niobium, previously annealed and outgassed, actually *increases* this slope. At the maximum solubility of oxygen (Nb+3.83 at.% O), $(\partial H_{cR}/\partial T)_{T\rightarrow T_c}$ has attained a value equal to -5000 Oe/deg. Meanwhile, in the same range of concentration the initial slope of the critical magnetic field $(\partial H_{cA}/\partial T)_{T\rightarrow T_c}$ remains essentially independent of concentration (Table I). Another interesting feature is that, although $(\partial H_{cR}/\partial T)_{T\rightarrow T_c}$ increases with interstitial oxygen or nitrogen concentrations [Figs. 8(a) and 8(b)], the corresponding peak magnetization and hysteresis loop (4.2°K) (Figs. 9 and 10) tend to decrease. Above the solubility limit, $(\partial H_{cR}/\partial T)_{T\rightarrow T_c}$ starts to decrease while the magnetization peak and hysteresis loop both increase. In other words, the magnetization data is not sensitive to changes in some yet undetermined residual microstructure, yet the resistometric results are widely influenced.

Similarly for the Nb-N system, when the interstitial is present in amounts approximating the solubility limit (e.g., Nb+0.33 at.% N), $(\partial H_{cR}/\partial T)_{T\rightarrow T_c}$ shows an increase over that evaluated for pure Nb. However, upon exceeding this concentration limit, the slope tends to continue to rise (rather than decrease, as is the case in the Nb-O system) with the magnetization peak and hysteresis loop (see below).

It may be concluded, then, that for the Nb-O and Nb-N solutions where the solute is present in amounts below the nominal solubility limit, the magnetic and resistometric data together indicate the presence of *both* a "mixed state" of the negative surface energy type of superconductor[6,7] and also some sort of "residual" substructure.[45] The exact nature of this substructure is not known but presumably could include interstitials present near dislocations and defects, spinodal structures, as well as segregation and precipitation at the lattice irregularities. This substructure seems to exhibit a higher critical field, H_{cR}, than that of the matrix, H_N.

To evaluate the *maximum* value of H_{cR}, it should be defined as the field required to restore *completely* the material to the normal state, R_n, and not to some arbitrary resistance like $R=0.5\ R_n$. This should be done with currents very small compared to the critical current. That is, resistive critical field should be measured not only at low current densities but should be evaluated at $R\rightarrow R_n$. In all likelihood this maximum critical field, $(H_{cR})_{R\rightarrow R_n}$, should be larger than H_N. It is interesting to compare H_N, determined from magnetic data at 4.2°K and $(H_{cR})_{R\rightarrow R_n}$. This may be illustrated for data obtained on solution, Nb+0.23 at.% N. If H_{cR} is evaluated at $R/R_n\rightarrow 1$ rather than $R/R_n=0.5$, a linear relationship with T is still apparent. When extrapolated to 4.2°K, it has a value equal to approximately 5.7 kOe compared to the value $H_N=5.0$ kOe. $(H_{cR})_{R\rightarrow R_n}$ similarly evaluated at 4.2°K for a specimen of Nb+1.43 at.% oxygen has a value 9.8 kOe compared to $H_N=9.4$ kOe. The smaller current densities in the resistive measurements than those cited here would tend to make these differences even larger.

A more direct as well as more striking comparison of $(H_{cR})_{R\rightarrow R_n}$ and H_N may be made simultaneously for niobium and the interstitial solutions by resistance transitions measured in transverse magnetic fields with the specimen carrying larger currents than reported here.[46,47] A more quantitative comparison of the relationship between $(H_{cR})_{R\rightarrow R_n}$ and H_N should, however, be made not only at the same temperature but near T_c

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[43] G. Bon Mardion, B. B. Goodman, and A. Lacaze, Phys. Letters **2**, 321 (1962).

[44] T. Kinsel, E. A. Lynton, and B. Serin, Phys. Letters **3**, 30 1962).

[45] K. Mendelssohn, Proc. Roy. Soc. (London) **A152**, 34 (1935).

[46] S. H. Autler, E. S. Rosenblum, and K. H. Gooen, Phys. Rev. Letters **9**, 489 (1962).

[47] W. DeSorbo, Bull. Am. Phys. Soc. **8**, 294 (1963).

where the Abrikosov theory is more applicable. H_N measured with greater precision than cited above might also reveal small but finite magnetization still present beyond this value. It would also be illuminating to investigate very high-purity single-crystal niobium and niobium with various known possible structures formed by spinodal decomposition,[48] and known molecular phases present.[20–23]

E. Magnetic Behavior and Critical Currents

The large hysteresis loops observed in niobium cold worked or niobium containing an interstitial concentration in excess of the solubility limit is consistent with the view defects or precipitates impede the free motion of flux filaments or "vortices"[6] in or out of the specimen in the mixed state as the field is increased or decreased leading to critical states[49,50] and magnetic hysteresis of the kind derived by Bean.[8] The latter analysis show that the distance of separation, $\Delta(4\pi M)$ at a given field, existing between the ascending and descending curves in the hysteresis loop is proportional to the current density, J_c, and radius, R, of the specimen. A qualitative correlation between $\Delta(4\pi M)$ and J_c may be seen by comparing the magnetization (Fig. 9) and critical current data (Fig. 11). If the solute concentration is below the solubility limit, both $\Delta(4\pi M)$ and J_c are small, but if the solute concentration is above the solubility limit, both $\Delta(4\pi M)$ and J_c tend to be large.

These results suggest that molecular species such as oxides and nitrides dispersed in niobium help to stabilize the super current vortices, in a manner perhaps similar to the influence of some large metal solutes in Nb.[5] No attempt has been made here to examine precipitate particle size and their degree of dispersion that would maximize the hysteresis loop and current carrying capacity presumably by rendering maximum pinning of the flux filaments.[50]

These preliminary results also seem to indicate that nonmetallic solutes, like oxygen or nitrogen, either present in the niobium lattice in interstitial positions or in some yet undefined substructure responsible for relative large resistive critical field at low current density do not seem to serve as effective stabilizers of the flux filaments in the "mixed state." They probably interact with the flux filaments at lower flux densities near H_{FP} where some irreversibility is observed in the magnetization curve.

SUMMARY

(1) The addition of interstitial oxygen solute atom to niobium lowers the transition temperature (resistive) approximately 0.93°K/at.%. At the solubility limit, approximately 3.83 at.%, $T_c = 5.8_4$°K, a decrease from 9.4_6°K for moderately pure niobium ($R_{298°\mathrm{K}}/R_{10°\mathrm{K}} \approx 500$). Above the solubility limit, T_c seems to rise again from the minimum value. The decrease in T_c in Nb is largest when oxygen is added. Oxygen has the largest solubility of the interstitials studied (nitrogen, hydrogen, and deuterium).

(2) The decrease in T_c due to interstitial additions to Nb is accompanied by an increase in lattice parameter. This correlation is inverse to that found for substitutional solid solutions of Nb and metallic solutes selected from Group IVA or VIA of the Periodic Table.

(3) Oxygen added to niobium, interstitially, increases the resistivity by approximately 5.2 $\mu\Omega$-cm/at.%.

(4) The magnetization behavior of niobium ($R_{298°\mathrm{K}}/R_{10°\mathrm{K}} \approx 500$) and similar specimens containing oxygen or nitrogen is substantially reversible and approximates the form predicted by Abrikosov for superconductors of the second kind. The field first penetrates the sample, macroscopically, at a value, H_{FP}, whose value is smaller than the thermodynamic critical field, H_c. As the concentration of the interstitial increases, H_{FP} decreases; while, H_N, the value of the field required to restore the superconductor to the normal state increases. The ratio H_N/H_c is a linear function of ρ_n, the resistivity in the normal state.

(5) When the solubility limit of the interstitial is exceeded, hysteresis loops become pronounced and are similar to those predicted by Bean's model.

(6) H_c for Nb determined from the area under the magnetization curve has a value 1520±20 Oe at 4.2°K; while at 0°K, it is estimated to be 1920±50 Oe. These values are in agreement with earlier H_c results obtained both from calorimetric and magnetic data.

(7) The coefficient of the electronic specific heat, γ, appears to be independent of the interstitial oxygen concentration.

(8) Niobium of purity indicated by resistance ratio, $R_{298°\mathrm{K}}/R_{10°\mathrm{K}} \approx 500$, and interstitial solid solutions derived from it still exhibit superconductivity detected resistometrically above H_N which is determined magnetically.

ACKNOWLEDGMENTS

The author wishes to thank R. W. Powers for valuable discussions concerning outgassing transition metals and preparation of their interstitial solid solutions. The use of his apparatus for this purpose is also gratefully acknowledged. The writer has benefitted from discussions with A. U. Seybolt, J. D. Livingston, H. R. Hart, Jr., and J. W. Cahn. Capable assistance was rendered in this work by W. A. Healy and G. E. Nichols to whom the author expresses his thanks. The first electron-beam melted niobium was prepared by H. W. Schadler and subsequent material provided by John Rutter and V. J. DeCarlo. Mrs. Theresa V. Brassard produced the optical micrographs. Lattice parameter of the solutions not previously reported were determined by Mrs. D. K. DeCarlo and Mrs. R. K. DiCerbo. The author is indebted to J. D. Livingston for helpful criticisms of the manuscript.

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[48] J. W. Cahn, Acta Met. **10**, 179 (1962).

[49] P. W. Anderson, Phys. Rev. Letters **9**, 309 (1962).

[50] J. Friedel, P. G. DeGennes, and J. Matricon, Appl. Phys. Letters **2**, 119 (1963).

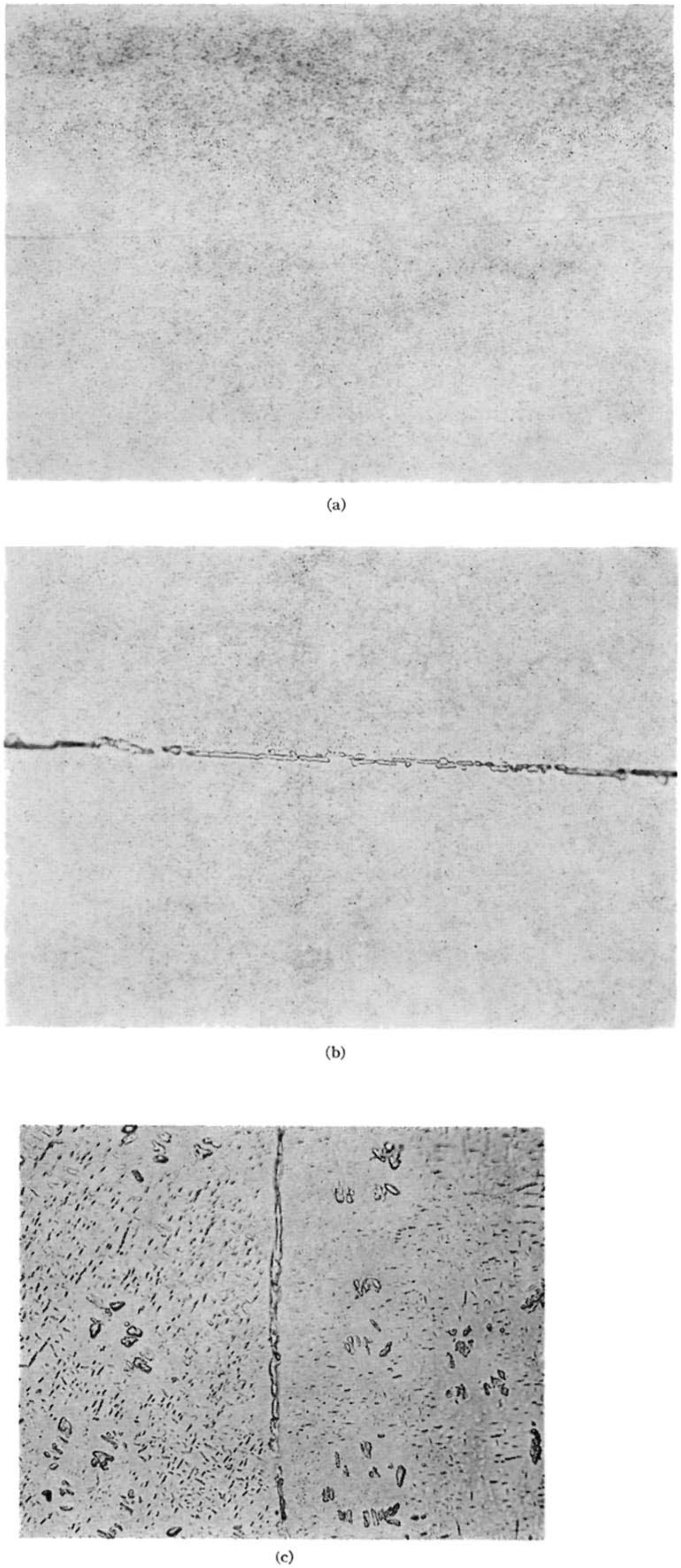
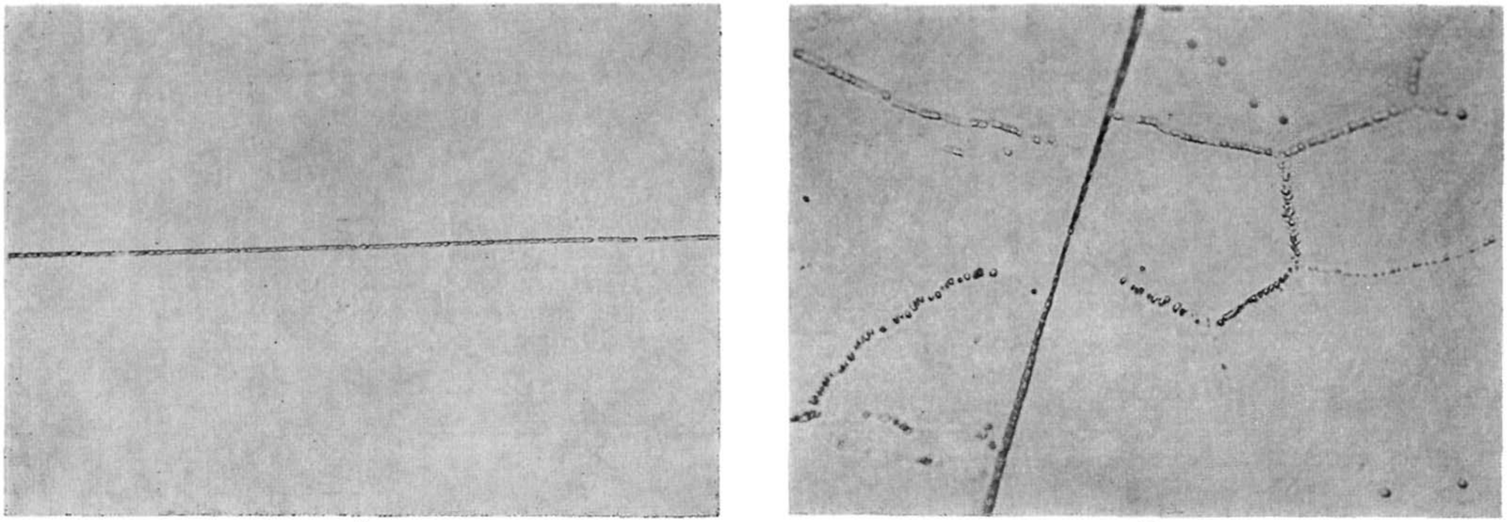
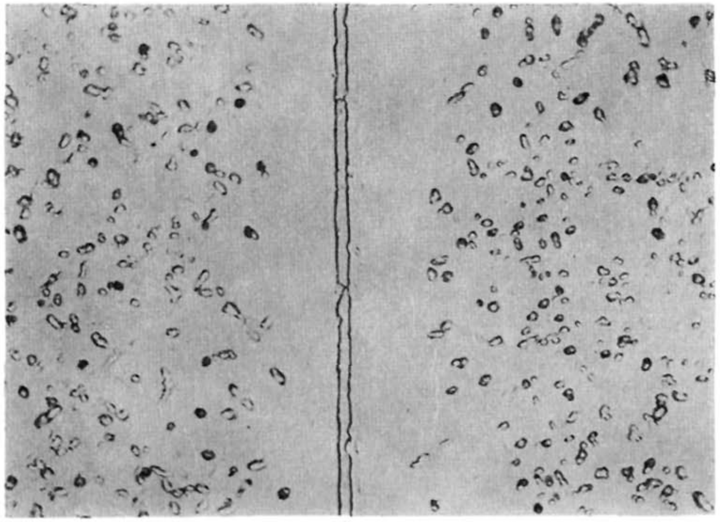


FIG. 4. Photomicrographs of niobium wires (0.029-in. diam). (a) Containing 5.18 at.% oxygen. Mag. 500×. No visible structure except in the grain boundary. Slow cooled (quenched in vacuum). (b) Containing 5.65 at.% oxygen. Mag. 500×. Possibly NbO in grain boundary (slow cooled). (c) Containing an apparent amount of 6.43 at.% oxygen. The small needle-like structure is probably a nitride, "Nb$_2$N," due to nitrogen contaminant. The other structure may be NbO. Mag. 1000×. (Slow cooled.)



(a)

(b)



(c)

FIG. 5. Photomicrographs of niobium wires (0.029-in. diam). (a) Containing 0.33 at.% nitrogen cooled in helium exchange gas. This concentration is close to the solubility limit. Discontinuous structure at grain boundary is probably "Nb_2N." (b) Containing 0.33 at.% nitrogen slow cooled (vacuum quenched). Note the tendency for the solute atom to concentrate at lattice irregularities such as low-angle and regular high-angle grain boundaries. Mag. 1000×. (c) Containing 1.64 at.% nitrogen (above the solubility limit) (slow cooled). Note the grain boundary is lined with nitride, probably "Nb_2N," and that the nitride is also within the grain with an apparent depletion near the grain boundary. Mag. 1000×.