

Size Factor and Superconducting Properties of Some Transition Metal Solutions*

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Superconducting primary substitutional solid solutions, consisting of niobium, vanadium or tantalum (column V of the periodic table) alloyed with a metal of column IVA or VIA, show interesting correlations between size of solute and (a) lattice parameter, (b) critical temperature, (c) critical current, (d) coefficient of electronic specific heat, and (e) the Debye characteristic temperature. Solute atoms larger than the matrix atoms increase (a), (b), (c), and (d), but decrease (e). Solute atoms smaller in size decrease (a), (b), (c), and (d), but increase (e). T_c is found to correlate better with an effective e/a ratio, that contains a size-dependent correction than with the usual e/a ratio. Magnetization studies indicate that these alloys approach an Abrikosov type of behavior when the sample is in powder form. In bulk form hysteresis is influenced by the relative size of solute and matrix atoms.

I. INTRODUCTION

AMONG the various factors mentioned in simple alloy theory¹ is the size factor; that is, the disparity in size² between the solute and solvent atoms. The influence of this on superconducting properties has not been singled out. It is not clear how a solute atom of different size, introduced in a lattice, influences such electronic properties as density of states at the Fermi level, range of coherence, and penetration depth, all important variables in the current understanding of high magnetic field, high current carrying superconductors. From structural considerations, when a large solute atom is introduced into a solid matrix, strain fields could result which could be responsible for a widespread disruption of the symmetry or regularity of the lattice with significant consequences on current carrying capacity, hysteresis effects, flux jumping, etc., of the superconductor. The electronic and structural properties are no doubt interdependent and to treat each separately would, indeed, be a poor approximation.

However, it is pointed out here that some superconducting primary substitutional solid solutions, consisting mainly of a transition metal, for example niobium, vanadium or tantalum, of column V of the periodic table alloyed with a metal of column IVA or VIA (body-centered cubic structures) show some interesting correlations between the size of the solute atom and (a) lattice parameter, a , (b) critical temperature, T_c , (c) critical current, I_c , (d) coefficient of electronic specific heat, γ , (e) Debye characteristic temperature, θ_D , (f) magnetization and hysteresis effects, (g) resistivity, and (h) an effective electron-atom ratio. For the most part, the results are consistent with the conclusions derived from a judicious use of the negative

surface energy model.^{3,4} The magnetic behavior of the bulk alloys with large solute atoms exhibiting pronounced hysteresis, are consistent with Bean's model.⁵

II. EXPERIMENTAL

The alloys were prepared by melting the metals in an arc furnace on a water-cooled copper hearth using a tungsten electrode. The alloy buttons were inverted and remelted several times in order to promote homogeneity. Rapid quenching of the melt in contact with the copper hearth occurred when the arc was extinguished. The wire specimens had a similar history of cold work. They were prepared by upset forging the cast button from which rods approximately 0.25 in. diam were cut, then swaged and drawn to the same size (0.030 in. diam). The preparation and heat treatment of the alloys was done by Hughes and Rockwood. The lattice parameters of the alloys not cited in the literature were determined with the Debye-Scherrer technique by Mrs DiCerbo and Mrs. DeCarlo.

The critical currents, I_c , were measured potentiometrically in a transverse magnetic field by methods similar to those already described.⁶ The fields were obtained by a small niobium wire (0.004 in. diam) wound iron core magnet designed and built by Hart, following an original design due to Autler.⁷ Maximum fields of 17 000 Oe were attained. The critical current of the wire specimen in a given field was that value which produced approximately 0.5 μ V across the two potential leads.

Magnetic induction measurements were carried out by a technique used earlier by Bean.⁸ The sample was flipped in an out of a copper coil (about 2 000 turns) coaxial with an external steady field. The coil was connected to a flux meter whose deflection was proportional

* This work was first reported in part at the American Physical Society meeting, Cleveland, 1962.

¹ L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals* (McGraw-Hill Book Company, Inc., New York, 1953), Chap. 4, p. 74.

² Atomic diameter is that assumed by Hume-Rothery [W. Hume-Rothery, *Atomic Theory for Students of Metallurgy* (The Institute of Metals, London, 1960), Chap. 15, p. 121.], namely, the closest distance of approach between two atoms in the crystal of the element.

³ A. A. Abrikosov, *Zh. Eksperim. i Teor. Fiz.* **32**, 1442 (1957) [Translation: *Soviet Phys.—JETP* **5**, 1174 (1957)].

⁴ B. B. Goodman, *IBM J. Res. Develop.* **6**, 63 (1962).

⁵ C. P. Bean, *Phys. Rev. Letters* **8**, 250 (1962).

⁶ J. E. Kunzler, *Rev. Mod. Phys.* **33**, 1 (1961).

⁷ S. H. Autler, D. B. Montgomery, and G. Ajootian, *Quarterly Progress Report on Solid State Research, Lincoln Laboratory, MIT, July 1960* (unpublished), p. 63.

⁸ C. P. Bean, Margaret V. Doyle, and A. G. Pincus, *Phys. Rev. Letters* **9**, 93 (1962).

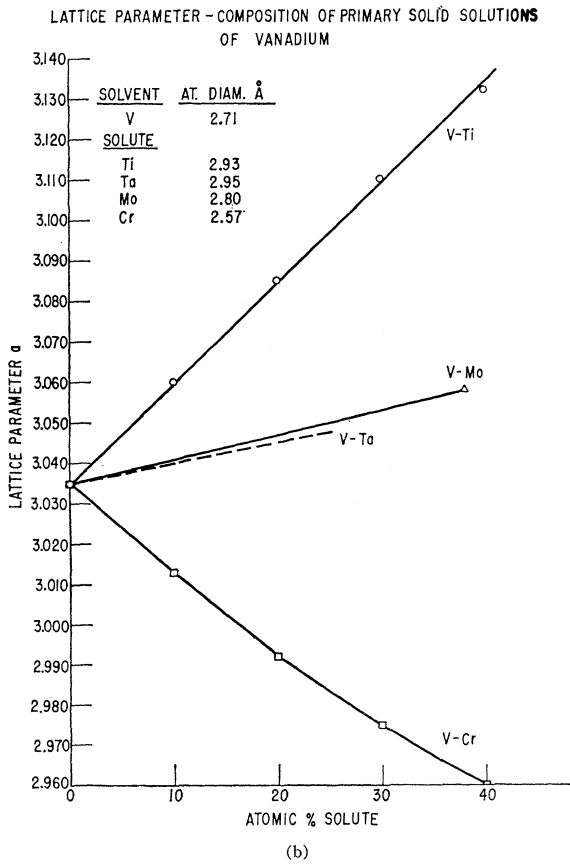
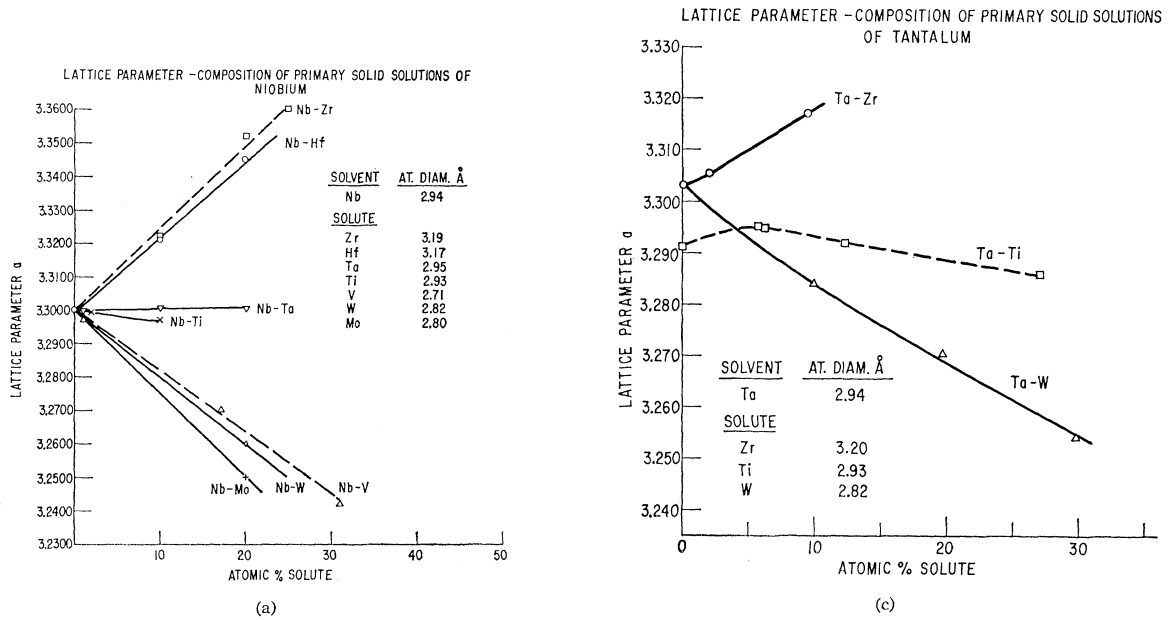


FIG. 1. Lattice parameter as a function of composition for primary solid solutions of (a) niobium, (b) vanadium, (c) tantalum, (d) reduced lattice parameter as a function of at. % solute for some Nb, V and Ta solid solutions.

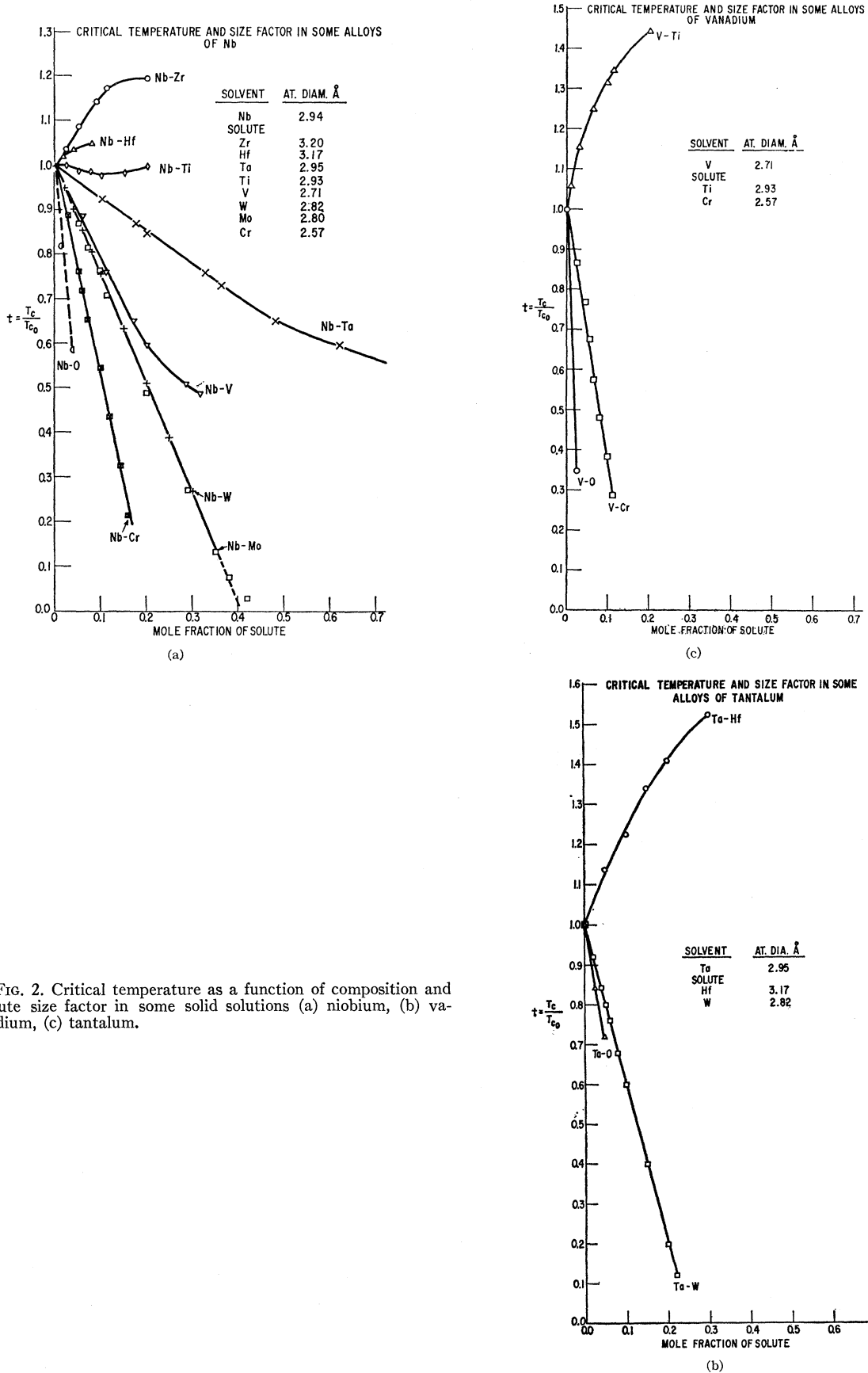


FIG. 2. Critical temperature as a function of composition and solute size factor in some solid solutions (a) niobium, (b) vanadium, (c) tantalum.

to the magnetization of the specimen. Magnetic field measurements were accurate to ± 10 Oe while $-4\pi M$ values were accurate to ± 5 G. The bulk specimens were about 0.6 cm in diameter and 1.2 cm long. The powder samples (particle size 45–60 μ) were "molded" into cylindrical shape of the same size with a paper "soda straw." Stopcock grease served as a binder while also insulating each particle.⁹ The small particles were obtained from the bulk specimen with a carboly cutting tool in an inert atmosphere. They were sized by screening.

III. RESULTS AND DISCUSSION

A. Lattice Parameter

The lattice parameter variation as a function of concentration for some primary solid solutions of^{10–12} Nb, V, and Ta are summarized in Figs. 1(a), 1(b), and 1(c), respectively. In general, for the concentrations shown, Vegard's Law¹³ is obeyed. The influence of solute size is readily apparent. The rate of change of the lattice parameter with composition reflects the difference in atomic diameter between the solute and base metal, increasing with large solute atoms and decreasing when the solute atom is smaller than the solvent atom [Fig. 1(d)].

B. Critical Temperature

The influence of solute concentration on the critical temperature for alloys of the three base metals has been reported earlier by Hulm and Blaughier¹⁴ (see also reference 15). To show the influence of solute size, the data, selecting mostly solutes of columns IVA and VIA, are plotted in terms of reduced temperature, $t = T_c/T_{c0}$, versus composition in Figs. 2(a), (b),¹⁶ and (c) for Nb, V, and Ta alloys, respectively. T_{c0} refers to the transition temperature of the parent metal; while T_c is that of the alloy. The influence of interstitial solute, such as oxygen, on T_c measured earlier¹⁷ is also

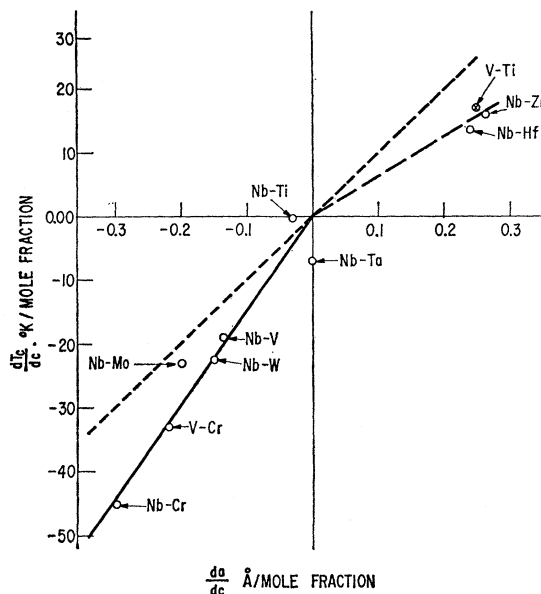


Fig. 3. The rate of change of critical temperature with composition, $(dT_c/dc)_{c \rightarrow 0}$ as a function of the rate of change of lattice parameter $(da/dc)_{c \rightarrow 0}$.

presented. For dilute homogeneous solutions, including in some cases concentrations greater than 0.1 atom fraction, the variation in transition temperature with composition of most of the binary systems is approximately linear. $(dT_c/dc)_{c \rightarrow 0}$ is positive when the solute atom is larger than the parent atom and negative when smaller. The correlation between $(dT_c/dc)_{c \rightarrow 0}$ and $(da/dc)_{c \rightarrow 0}$ is shown in Fig. 3. The results summarized in Figs. 1–3 demonstrate the direct correspondence that exists between the substitutional solute size, lattice parameter and critical temperature.

It may be generalized that for these dilute solutions, if the alloying element has an atomic diameter greater than that of the base metal, both the lattice parameter (or molar volume) and the transition temperature increase with increasing amount of solute atom. However, if the alloying element has an atomic diameter smaller than that of the base metal, both the lattice parameter and the transition temperature decrease with increasing amount of solute atom. The exceptions are niobium-rich tantalum alloys where the solute is in column V; although niobium-rich vanadium alloys show the effect. For dilute interstitial homogeneous solid solutions of the same transition base metals, the lattice parameter is increased by the interstitial solute but the transition temperature is found to decrease.¹⁷ Generally, if the atomic volume of metals is decreased by elastic compression, the transition temperature is lowered and, conversely, tension usually will raise it.¹⁸

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

¹⁰ Nb-Zr, B. A. Rogers, and D. F. Atkins, J. Metals **7**, 1034 (1955). Nb-Ta, H. Bückle, Z. Metallk. **37**, 53 (1946). Nb-Hf, R. K. DiCerbo and D. K. DeCarlo (private communication). Nb-Ti, M. Hansen, E. L. Kamen, H. D. Kessler, and J. D. McPherson, Trans. AIME **191**, 881 (1951). Nb-V, H. A. Wilhelm, O. N. Carlson and J. M. Dickinson, *ibid.* **200**, 915 (1954). Nb-W, Nb-Mo, H. Bückle, Z. Metallk. **37**, 53 (1946).

¹¹ V-Ti, V-Mo, V-Cr, V-Ta, W. Rostoker, *The Metallurgy of Vanadium* (John Wiley & Sons, Inc., New York, 1958), p. 38.

¹² Ta-Ti, D. Summers-Smith, J. Inst. Metals **81**, 73 (1952). Ta-W, C. H. Schramm, P. Gordon, and A. R. Kaufmann, J. Metals **2**, 195 (1950); Ta-Zr, D. K. DeCarlo and R. K. DiCerbo (private communication).

¹³ L. Vegard, Z. Physik **5**, 17 (1921); L. Vegard and H. Dale, Z. Krist. **57**, 148 (1928).

¹⁴ J. K. Hulm and R. D. Blaughier, Phys. Rev. **123**, 1569 (1961).

¹⁵ Jean Müller, Helv. Phys. Acta **32**, 141 (1959); E. Bucher and J. Müller, *ibid.* **34**, 410 (1961).

¹⁶ V+33 at. % Zr, $T_c = 8.80^\circ\text{K}$ [B. T. Matthias, V. B. Compton, and E. Corenzwit, J. Phys. Chem. Solids **19**, 130 (1961).] is not included.

¹⁷ W. DeSorbo and G. E. Nichols, Bull. Am. Phys. Soc. **6**, 267 (1961), and unpublished data.

¹⁸ D. Schoenberg, *Superconductivity* (Cambridge University Press, New York, 1960), 2nd ed., pp. 10, 73–77.

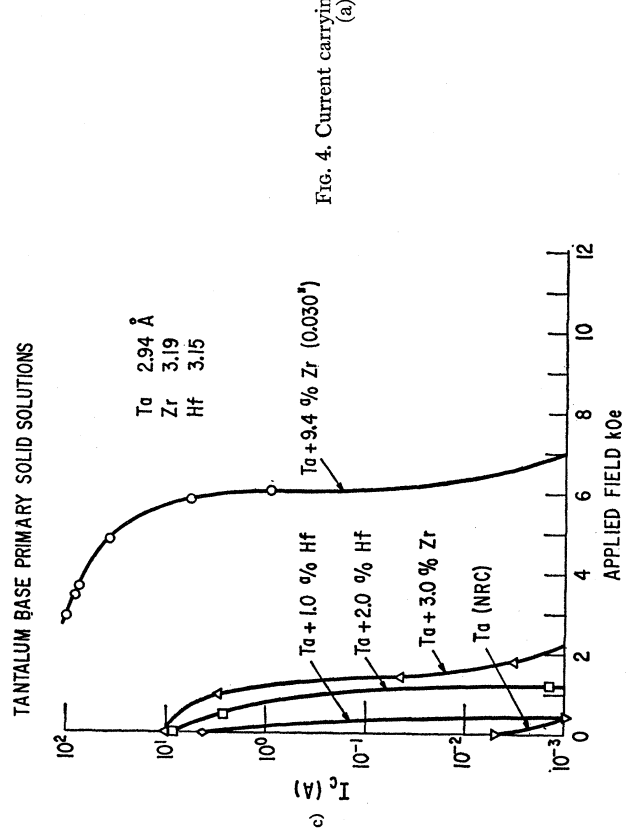
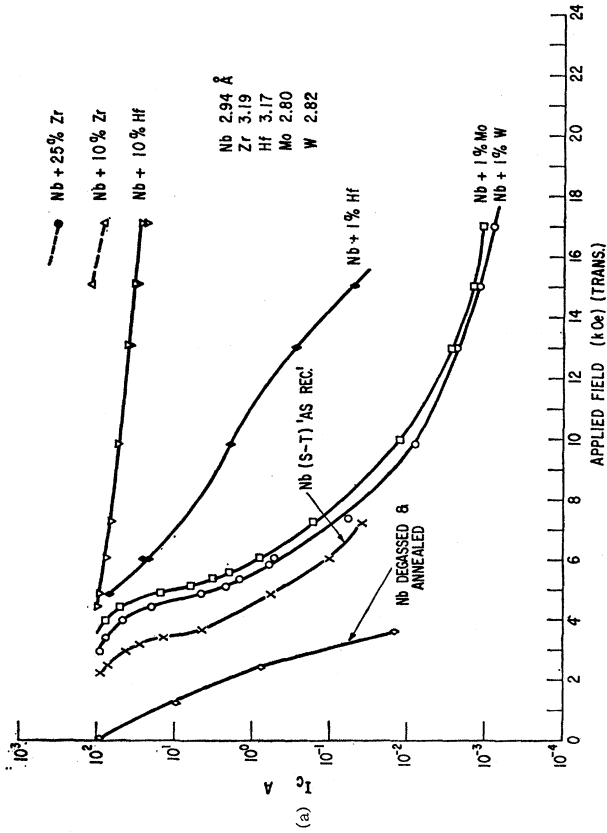
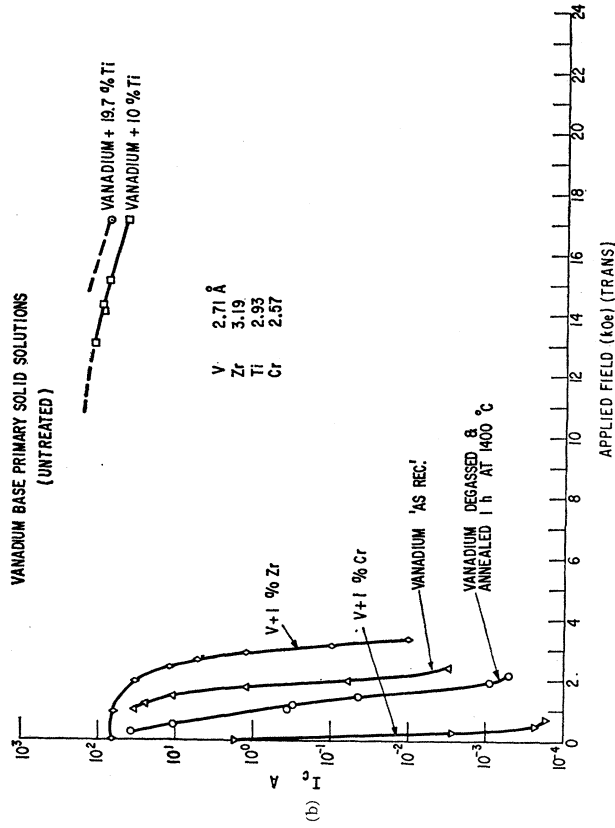


Fig. 4. Current carrying capacities as a function of applied field illustrating the influence of solute size for alloys of (a) niobium, (b) vanadium, (c) tantalum (0.030 in. diam wire, $T=4.2^\circ\text{K}$.)

C. Critical Current in Transverse Magnetic Fields

The current carrying capacities of some of the alloys characterized according to solute size are illustrated in Figs. 4(a), (b), and (c) for each of the three base metals Nb, V and Ta, respectively. The results are compared in each case with the corresponding base metal. The percent reduction of the cross sectional area of each wire (0.030 in. diam) is constant. At larger fields, the current carrying capacity of the alloy goes up with increasing concentration of the solute that has a larger atomic diameter than the base metal. In the Nb-base alloys and in fields above approximately 12 000 Oe, the addition of 1 at. % Hf to niobium makes the metal a better current carrier than niobium containing 1 at. % W or 1 at. % Mo. Note the similarity in the I_c vs H curve characteristic of these latter two solutions. Both solute atoms are similar in size. Their influence on the critical temperature of niobium are also strikingly similar [Fig. 2(a)]. For larger concentration the influence of solute size on current carrying capacity is also apparent at the higher fields. Niobium containing 10 at. % Zr is, for example, a better current carrier than niobium containing 10 at. % Hf at 17 000 Oe.

D. The Coefficient of the Electronic Specific Heat, γ and the Debye Characteristic Temperature, θ_D

The variations in γ and θ_D with concentration and solute size in the transition metal solutions of interest in this paper can be illustrated from the low temperature calorimetric data recently published on three alloy systems, V-Ti,¹⁹ V-Cr,²⁰ and Nb-Mo.²¹ In the V-Ti system, where the solute atom is large, γ is found to increase with concentration; whereas, θ_D decreases with concentration. In the alloys, V-Cr, and Nb-Mo, γ decreases while θ_D initially increases with concentration of the solute atom whose atom size is smaller than the parent atom. These variations in γ and θ_D with solute atom size are illustrated in Fig. 5(a) for V-Ti and Fig. 5(b) for V-Cr.²² Also summarized are the variations with concentration of T_c , I_c (measured in a transverse field of 17 000 Oe for a 0.030 in. diam wire), molar volume (calculated from lattice parameters) and the interaction parameter term, V , (evaluated for both V-Ti and for V-Cr by Cheng *et al.*¹⁹). The approximate

¹⁹ C. H. Cheng, K. P. Gupta, E. C. van Reuth, and P. A. Beck, *Phys. Rev.* **126**, 2030 (1962).

²⁰ C. H. Cheng, C. T. Wei, and P. A. Beck, *Phys. Rev.* **120**, 426 (1960).

²¹ E.g., see R. D. Blaugher, J. K. Hulm, J. A. Rayne, B. W. Veal, and R. A. Hein, in *Proceedings of the Eight International Conference on Low Temperature Physics*, London, September, 1962 (unpublished).

²² Although the solute atom is not in group IV A or VI A, the alloy system, Nb-Ru, whose low temperature calorimetric data has recently been reported [E. Bucher, J. Muheim, and J. Müller, in *Proceedings of the Eighth International Conference on Low Temperature Physics*, London, 1962 (unpublished)], and whose solute is smaller in size than the solvent, γ and θ_D vary in the same manner as that observed in V-Cr and Nb-Mo.

correspondence between the maximum in T_c and γ , or the density of states, has been discussed by Hulm and Blaugher.^{14,22a}

E. Magnetization and Hysteresis

The influence of solute size on the magnetization and hysteresis for these transition metal solutions is illustrated in Fig. 6 for three niobium base alloys, in bulk form, where the solute atom is (a) larger (Nb-Zr), (b) approximately the same (Nb-Ti), and (c) smaller (Nb-W) than the parent atom. The concentration of the solute in each case is about 9–10 at. %. The measurements were made at approximately the same reduced temperature, i.e., $t \approx 0.40$, up to an applied field of about 7000 Oe. The peak magnetization and hysteresis loop are larger when the solute atom is larger than the parent atom. These large effects may also be observed in other binary, single-phase, homogeneous alloys containing large solute atom, e.g., vanadium-rich titanium (Fig. 7) and tantalum-rich zirconium alloys. The peak magnetization and hysteresis loop are smaller when the solute atom size is approximately the same as that of the solvent atom. Other examples showing similar magnetic behavior in this class are the niobium-tantalum alloys.²³ For alloy systems consisting of solute atoms smaller than the solvent atom, for example, single phase homogeneous niobium-rich tungsten, tantalum-rich tungsten, vanadium-rich tungsten, the peak magnetization and hysteresis loop are still smaller, comparable to that observed when the specimen is in powder form.

The influence of concentration on the magnetic behavior for a given solute size has been studied in vanadium-rich titanium alloys where the solute atom is larger than the solvent atom. The results are summarized in Fig. 7 for three alloys and for vanadium with a resistance ratio, $R_{300^\circ\text{K}}/R_{10^\circ\text{K}} \approx 100$. Disregarding "flux-jumping" effects, an increase in concentration of the large solute atom tends to increase both the peak magnetization and hysteresis loop for the compositions shown. In this range the frequency of "flux-jumping" tends to increase with solute concentration when the measurements are made under the same experimental conditions and procedure (e.g., rate of field increase or decrease is the same). "Flux-jumping" is not observed, at fields up to 7000 Oe., in the alloys whose solute size is either approximately the same (Nb_{0.64}Ta_{0.36}, Nb_{0.9}Ti_{0.1}) or smaller (Nb_{0.9}W_{0.1}) than the solvent atom. These observations are consistent with the findings of Kim *et al.*²⁴

When the specimens are in powder form, both the peak magnetization and the hysteresis loop are smaller than that observed in the corresponding bulk specimen,

^{22a} Note added in proof. For the original suggestion for this correspondence see D. Pines, *Phys. Rev.* **109**, 280 (1958).

²³ A. Calverley and A. C. Rose-Innes, *Proc. Roy. Soc. (London)* **A255**, 267 (1960).

²⁴ Y. B. Kim, C. F. Hempstead, and A. R. Strnad, *Phys. Rev.* **129**, 528 (1963).

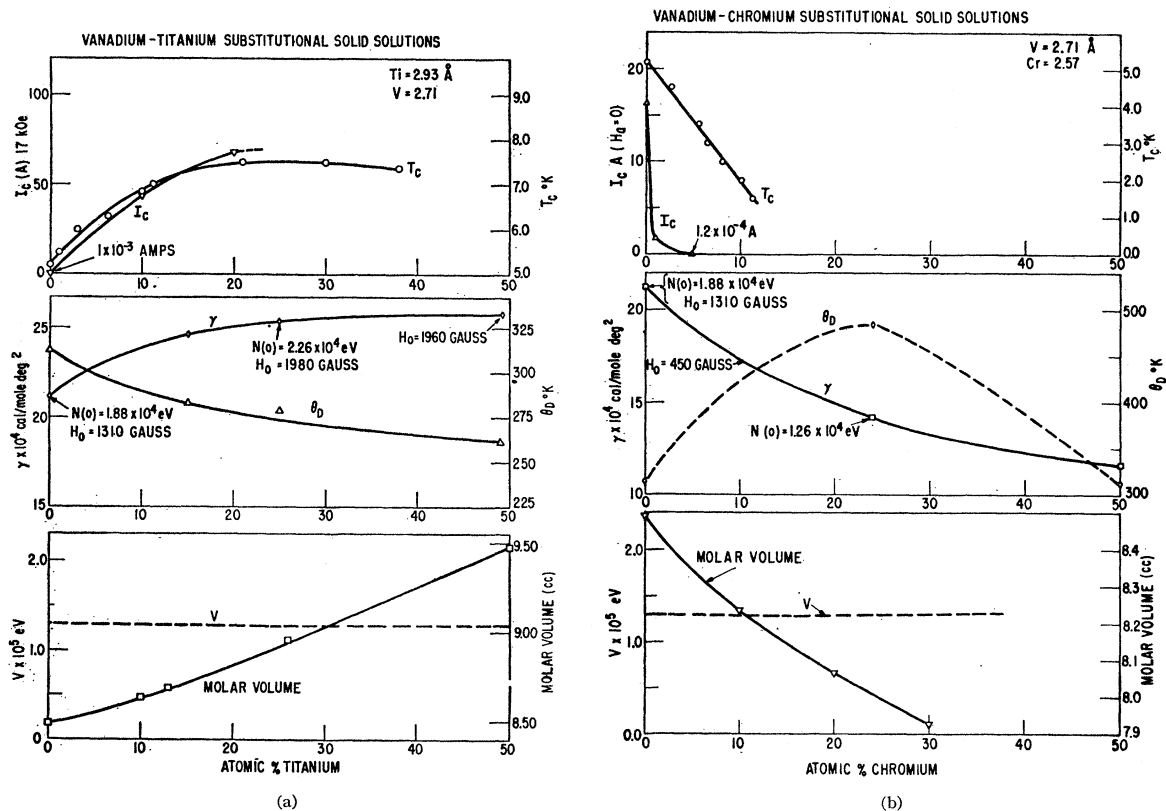


FIG. 5. The correlation at 4.2°K of critical current (17 kOe, transverse) T_c , γ , θ_D , molar volume, and interaction parameter (V) in V-Ti and V-Cr substitutional solid solutions with concentration and solute size.

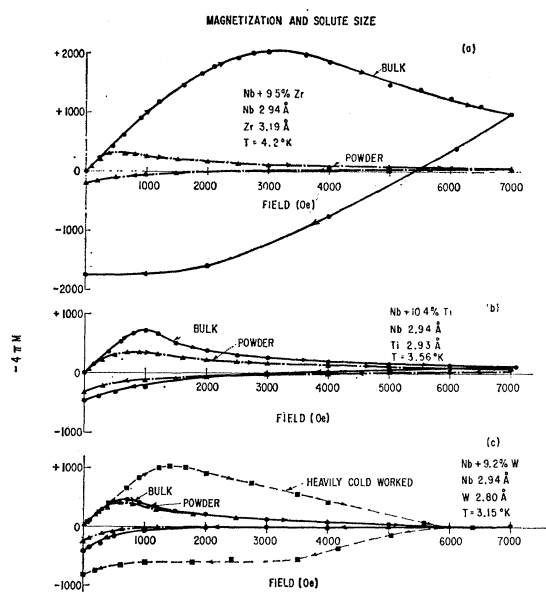


FIG. 6. Magnetization (G) vs applied field (Oe) of alloys (a) Nb+9.5 at. % Zr, (b) Nb+10 at. % Ti, and (c) Nb+9.2 at. % W, showing the influence of solute size. The results are shown for both bulk (rods 1.2 cm long, 0.6 cm diam) and powder (particle size 45-60 μ) samples.

appearing to be unaffected by the relative size of the solute and solvent atoms (see Figs. 6 and 7). The magnetization loops tend to be more asymmetric approaching the magnetic behavior predicted by negative surface energy models.^{3,4} The predicted curve for a negative surface energy superconductor is reversible. The applied field first penetrates the specimen at a field, H_{FP} , smaller than the thermodynamic field, H_c . The normal state is achieved at a field, $H_N > H_c$ (Fig. 8).

It is interesting to compare the magnetization data obtained on some of the bulk specimens with an analysis discussed by Goodman (see Fig. 2, reference 4). The alloys selected are those exhibiting relatively small hysteresis loops; or those whose solute atom is either the same or smaller in size than the solvent atom. For convenience, the concentration of the solute in the alloy is such that $-4\pi M$ becomes zero at an applied field equal to or less than 7000 Oe. Assuming that the ascending magnetization curve is similar to the theoretical curve for a negative surface energy superconductor and ignoring the hysteresis loop, H_c is then approximated from the area under the experimental curve.^{25,26}

²⁵ J. D. Livingston, Phys. Rev. **129**, 1943 (1963).

²⁶ T. F. Stromberg and C. A. Swenson, Phys. Rev. Letters **9**, 370 (1962).

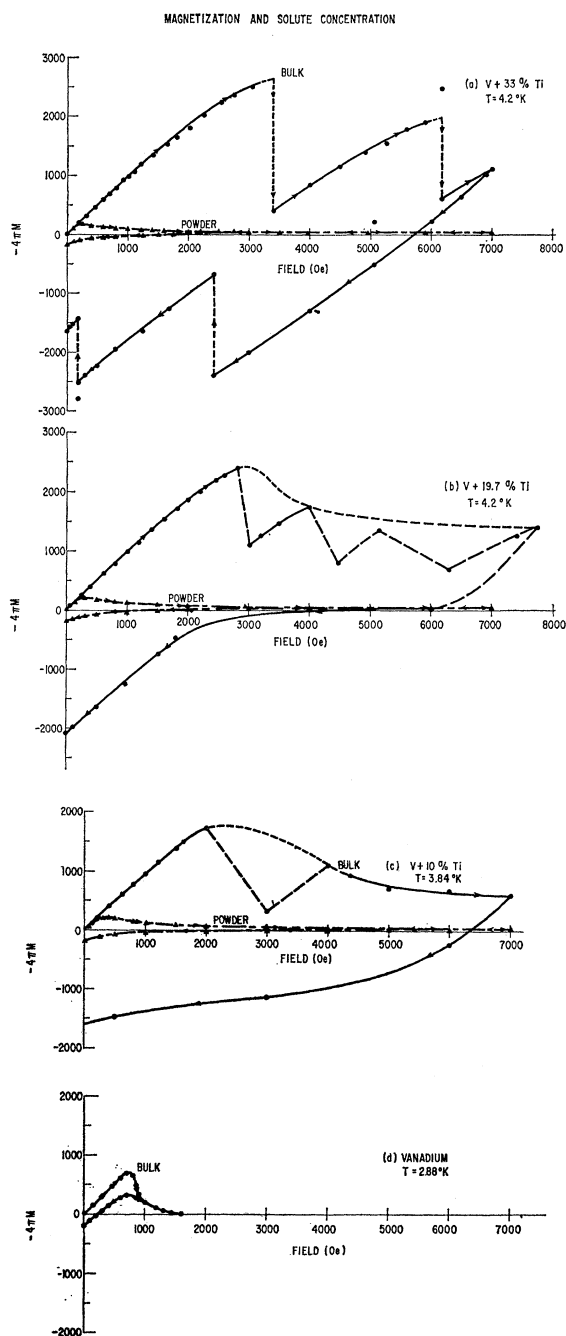
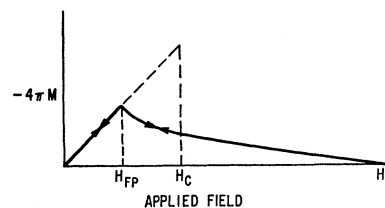


FIG. 7. The influence of solute (large) concentration on the magnetic behavior for some V-Ti solid solutions; measurements at approximately the same reduced temperature ($t \approx 0.55$). Discontinuities represent "flux jumping." The results are shown for both bulk (rod 1.2 cm long, 0.6 cm diam) and powder (particle size 45–60 μ) samples.

H_N is taken equal to the applied field required to transform the specimen to the normal state ($-4\pi M = 0$). H_{FP} is taken to correspond to the field represented by the interception of the experimental curve, extrapolated back from the higher fields, to the line where $-4\pi M$

FIG. 8. The magnetization curve for a "negative surface energy" superconductor (see reference 4).



and applied fields are equal. The data plotted in terms of $h_1 = H_{FP}/H_c$ vs $h_2 = H_N/H_c$, evaluated at 4.2°K (Fig. 9), show satisfactory agreement with Abrikosov's interpolated curve.⁴ Results obtained on some interstitial solid solutions of niobium as well as pure niobium^{26,27} and vanadium²⁸ are also included. An attempt has also been made to analyze the data available on the V-Ti system. In the three alloys shown, H_{FP} was evaluated at 4.2°K from data obtained on powder specimens (Fig. 7), while H_N was that observed on bulk specimens at 1.2°K by Berlincourt and Hake.²⁹ H_c was calculated at 4.2°K from the parabolic relationship³⁰ between H_c and T^{31} and the similarity principle proposed by the BCS theory (Eq. 3.40, reference 32). The coefficient of the electronic specific heat values, γ , required in the calculation were obtained from the data of Cheng *et al.*¹⁹ The results of this analysis for the three V-Ti alloys included in Fig. 9 appear to be in better agreement with Goodman's laminar model.⁴ However, if one assumes that h_2 decreases as T_c is approached³³ and that h_1 does not change appreciably with temperature,^{26–28} a temperature correction applied to h_2 could bring the points in closer agreement with the Abrikosov curve.

Another experimental result interpreted in terms of negative surface energy superconductors is the apparent independence of H_N on cold work²⁹ as shown in Fig. 6(c).

It is, therefore, suggested, with the evidence now at hand, that homogeneous, single phase binary transition metal solutions of Nb, V, or Ta, reported here, and classified according to size factor, are basically negative surface energy superconductors. The deviations from this behavior, for example, magnetization curves with large hysteresis loops, are observed, in general, in those alloys where the solute atom size is greater than that of the solvent. For these materials the magnetic behavior seems to be consistent with that treated by Bean⁵ as expected from Mendelssohn's filamentary model.³⁴ In

²⁷ W. DeSorbo, Bull. Am. Phys. Soc. **8**, 79 (1963).

²⁸ W. DeSorbo and W. A. Healy (unpublished).

²⁹ T. G. Berlincourt and R. R. Hake, Phys. Rev. Letters **9**, 293 (1962).

³⁰ Investigations carried out on some dilute vanadium alloys (reference 15), high purity Nb (references 26, 27) and V (reference 28) show this relationship to be a good approximation for these materials.

³¹ See reference 18.

³² J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

³³ E. A. Shapoval, Zh. Eksperim. i Teor. Fiz. **41**, 877 (1961) [translation: Soviet Phys.—JETP **14**, 628 (1962)].

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

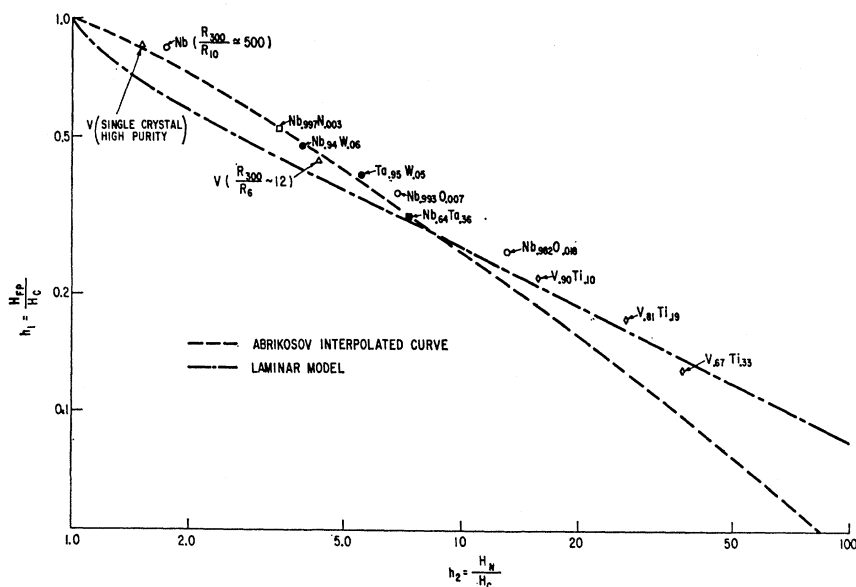


FIG. 9. The relation between two reduced transition fields compared to Abrikosov's theory and Goodman's laminar model (reference 4).

Bean's model the hysteresis loop or the extent of separation, ΔH , between the ascending and descending magnetization curves, is proportional to the current density, J_c , and to the radius of the specimen, R . In this class of alloys, both ΔH and J_c are increased by increasing the solute size. This may be seen in a qualitative manner, by inspecting Figs. 4(a) and 6, or Figs. 4(b) and 7. The size-dependent contribution to the total magnetization loop in the bulk specimen obscures the intrinsic magnetization.^{9,35} As suggested earlier, the introduction of a large solute atom into the lattice may disrupt the regularity creating local or extended flaws³⁶; atom clustering^{37,38} could also occur. These changes in the lattice could give rise to some spatial modulation of the free energy between the normal and superconducting phases.^{39,40} They could also serve as barriers to the thermally activated motion of flux lines.⁴¹

F. Resistivity

The resistivity of an alloy is influenced by the square of the valence difference between the solute and solvent atoms.⁴² The influence of solute size on the resistivity is illustrated in Fig. 10(a) and (b) for the base metals niobium and tantalum, respectively. The solutes, hafnium and titanium, have the same valence, smaller by one from that of the parent atom. For a given concentration of solute, the one having the larger atomic

diameter, enhances the resistivity of the alloy⁴³ more. In any event, for dilute solutions, solute concentrations less than approximately 0.05 atom fraction, the resistivity increase due to the addition of a substitutional solute is smaller than that brought about by the same concentration of an interstitial solute atom such as oxygen.

G. Effective Electron-Atom Ratio

The electron-atom ratio, N , defined as the number of valence electrons per atom considering all the electrons outside a filled shell, has been used to establish empirical rules for the occurrence of superconductivity.^{44,45} If one substitutes a solute atom containing an extra electron, this fills the electron energy bands to a slightly higher energy. One is assuming that the superconducting properties depend on the height to which the energy bands are filled.

In the theory of electrical resistivity, if a solute atom is larger than the solvent, the lattice is expanded locally, i.e., it has a reduced ion charge locally; and, therefore, the region behaves as if the solute had lower valence than in the undistorted case. As mentioned earlier, the resistivity tends to vary as the square of the difference between the solute and solvent valence. The effective valence should be used for the solute valence in this relation. The influence of this on resistivity can be appreciated by comparing the resistivity of Nb-Ti with

³⁵ J. J. Hauser, Phys. Rev. Letters **9**, 423 (1962).

³⁶ W. DeSorbo, Suppl. J. Appl. Phys. **34**, 1378 (1963).

³⁷ R. L. Fleischer (private communication).

³⁸ R. L. Fleischer, Phys. Letters **3**, 111 (1962).

³⁹ C. J. Gorter, Phys. Letters **2**, 26 (1962); **1**, 69 (1962).

⁴⁰ L. T. Claiborne and N. G. Einspruch, Phys. Rev. Letters **10**, 49 (1963).

⁴¹ P. W. Anderson, Phys. Rev. Letters **9**, 309 (1962).

⁴² N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958).

⁴³ The resistivity data of the substitutional solid solutions Nb-Hf, Nb-Ti, Ta-Hf, and Ta-Ti is that of T. G. Berlincourt and R. Hake (unpublished). The author is grateful to them for permission to use the data prior to publication.

⁴⁴ B. T. Matthias, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam 1957), Vol. II, p. 138.

⁴⁵ B. T. Matthias, T. H. Geballe, and V. B. Compton, Rev. Mod. Phys. **35**, 1 (1963).

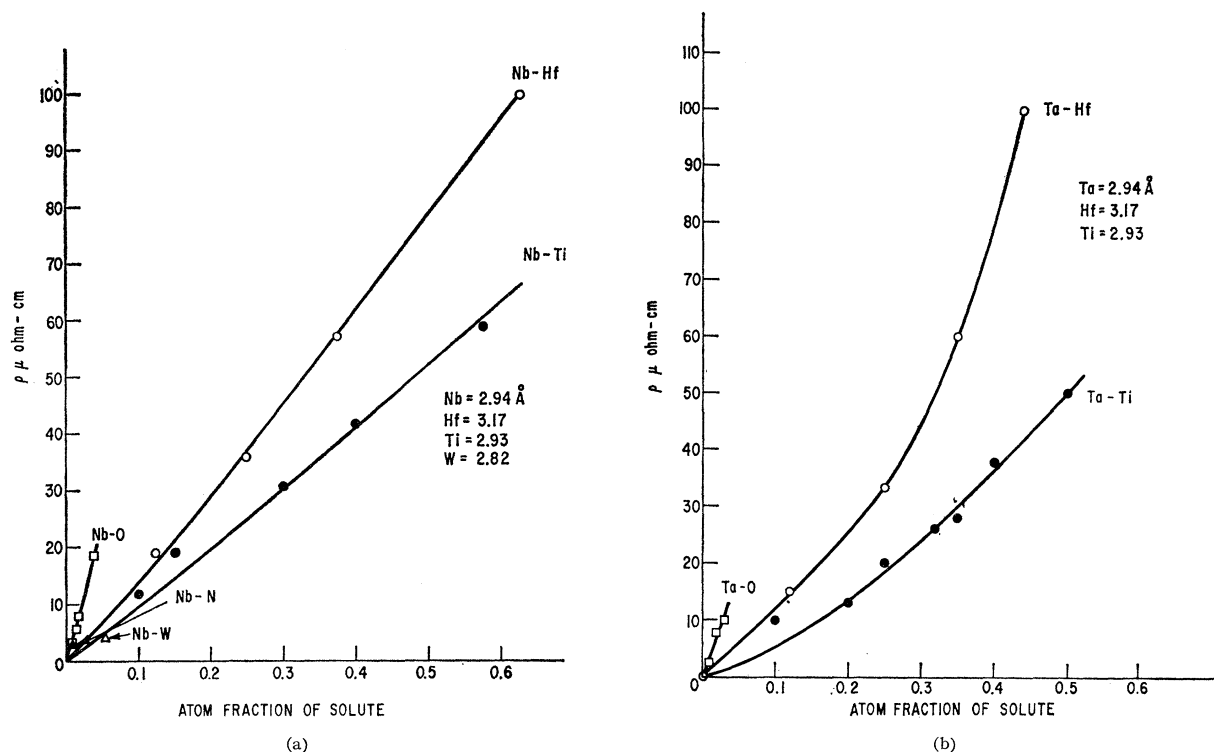


FIG. 10. The influence of solute size on the resistivity at 1.2°K (a) niobium and (b) tantalum solutions. The solute atoms, Hf and Ti, each have the same valence, one smaller than the parent atom. Data for substitutional solid solutions Nb-Hf, Nb-Ti, Ta-Hf, and Ta-Ti were obtained from Berlincourt and Hake (reference 43). Resistivity data for Nb-O and Ta-O solutions were obtained at 10°K (reference 17).

Nb-Hf or Ta-Ti with Ta-Hf alloys [Figs. 10(a) and (b)] at the same concentration. Thus, a solute has an effective valence, Z^* , given by its true valence, Z , plus a volume correction⁴⁶

$$Z^* = Z - (\delta V/V)Z_0, \quad (1)$$

where δV is the local change in volume, V is the original cell volume and Z_0 is the valence of the solvent. One could say that this expanded region soaks up some extra electrons, reducing the electron concentration in the matrix. Harrison⁴⁷ has suggested carrying this concept over to the superconducting case where the value for N in the matrix now takes the form

$$N = [A]Z_0 + [B]Z^* \quad (2)$$

or to a change in N with the addition of the solute of

$$\delta Z = N - Z_0 = [B] \left[(Z - Z_0) - \frac{\delta V}{V} Z_0 \right], \quad (3)$$

where A and B represent the atom fraction of solvent and solute, respectively.

Matthias^{44,45} also suggested a dependence of T_c upon volume by writing

$$T_c \propto V^{\alpha} f(N). \quad (4)$$

⁴⁶ F. J. Blatt, Phys. Rev. **108**, 285 (1957).

⁴⁷ W. A. Harrison (private communication).

This approach regards the variation with volume as independent of the variation with N . The mechanism suggested by Harrison gives a specific form for the volume dependence. An improvement in the correlation δZ with T_c with this latter scheme is shown in Fig. 11 for a series of niobium solid solutions.

IV. SUMMARY

(1) The variation in the lattice parameter, a , for some dilute primary homogeneous solid solutions of Nb, V, Ta alloyed with metals of Column IVA or VIA of the periodic table, in general, follow Vegard's law. a increases with concentration of a solute atom whose diameter is larger than the solvent atom and decreases with concentration when it is smaller.

(2) If the alloying element has an atomic diameter greater than that of the base metal, the superconducting transition temperature increases with increasing amount of solute for the dilute primary substitutional solid solutions. However, if the alloying element has an atomic diameter smaller than that of the base metal, the transition temperature decreases with increasing amount of solute atom.

(3) At high magnetic fields, e.g., greater than 12 000 Oe for dilute homogeneous niobium-base alloys, the current-carrying capacity of an alloy goes up with in-

THE CHANGE IN ELECTRON-ATOM RATIO, δZ , AND T_c WHEN 10% SOLUTE IS ADDED TO NIOBIUM

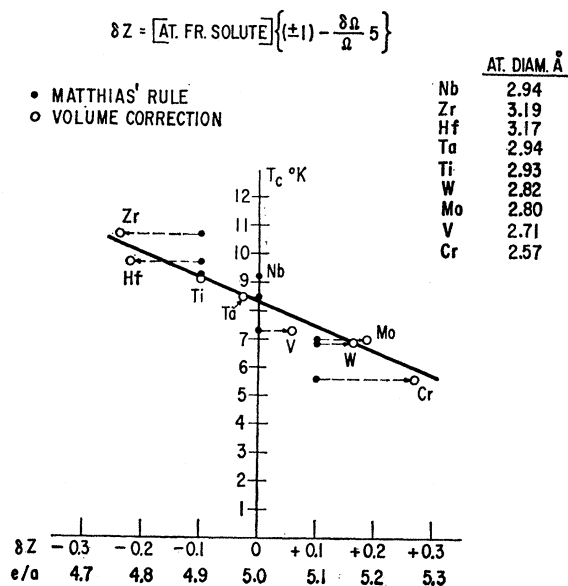


FIG. 11. The change in electron-atom ratio with and without solute size-dependent corrections compared to the critical temperature for some solid solutions of niobium.

creasing concentration of a solute that has a larger atomic diameter than the base metal. A similar correspondence may be seen for dilute vanadium or tantalum-base alloys.

(4) For dilute alloys whose solute atom size is larger than the solvent atom, the coefficient of the electronic

specific heat, γ , increases with composition; whereas, the Debye characteristic temperature, θ_D , decreases with composition.

(5) The magnetization of dilute homogeneous solid solutions with solute atoms about the same size or smaller than the solvent atom is that predicted by "negative surface" energy models whether the material is in bulk form or in a finely divided state. For solutions consisting of a large solute atom this behavior is seen only when the material is in a finely divided state. It is concluded that all of these transition metal solutions are basically "negative surface energy" superconductors. For bulk samples of alloys with large solute atoms, hysteresis effects are dominant, concealing the negative surface energy behavior. This magnetic behavior and the large current carrying capability of these materials are consistent with Bean's model.

(6) T_c is found to correlate better with an effective e/a ratio, which contains size-dependent correction than with the usual e/a ratio.

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