

# Superconducting Solid Solution Alloys of the Transition Elements

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The solid solution alloys formed by the incomplete  $d$ -shell metals in groups 4, 5, 6, and 7 have been tested for superconductivity down to 1°K. For alloys formed between neighboring elements in a given row of the periodic table, two transition temperature maxima are observed with valence numbers approximately equal to 4.7 and 6.4, respectively, the only exception being the first long period, in which the upper maximum is absent. Similar maxima occur when the constituent elements are selected from different rows of the periodic table, thus confirming the dominant role of the  $d$ -shell electrons. It is known that the normal density-of-states function,  $N(0)$ , passes through a series of maxima as the  $d$ -shell is filled up, two of these peaks lying at about the same composition as the two transition temperature peaks observed in the present work. The relationship of  $T_c$  to  $N(0)$  for the transition metal alloys is discussed. Transition temperature data are also presented for alloys composed of neighboring elements in a given column of the periodic table. In this case, the form of the relationship between  $T_c$  and electronic or lattice properties is still obscure.

## I. INTRODUCTION

IN spite of recent advances in the fundamental theory of superconductivity, we are still unable to make a reliable prediction of the superconducting transition temperature,  $T_c$ , of any given material from basic knowledge of its lattice and electronic properties. According to the theory of Bardeen, Cooper, and Schrieffer<sup>1,2</sup> (referred to hereafter as BCS),  $T_c$  is connected exponentially with the density of states at the Fermi surface and an interaction parameter between electrons which lie close to that surface. An accurate calculation of  $T_c$  using this relationship appears to be difficult and does not seem to have been attempted for any specific material.

Starting from an experimental viewpoint, several attempts have been made to obtain an empirical expression for  $T_c$ . For the nontransition metal superconductors with closed  $d$  shells, Daunt<sup>3</sup> and Lewis<sup>4</sup> pointed out that  $T_c$  is roughly proportional to the coefficient of the electronic heat capacity,  $\gamma$  (or  $\gamma$  raised to a very low power, e.g.,  $\gamma^{1.2}$ ), where this coefficient is itself directly proportional to the density of states at the Fermi surface. No corresponding relationship is available for the superconducting transition elements, that is, for many of the metals with incomplete  $d$  shells ranging from group 3A to group 8A of the periodic table, except that in this case also  $T_c$  tends to increase for increasing values of  $\gamma$ . As a matter of fact, the rate of increase is approximately three times greater for the transition metals than for the nontransition metals, a result for which no explanation has yet been offered. A further mysterious fact is the failure of several transition elements of the platinum group to exhibit superconductivity, even though their  $\gamma$  values appear to be more than large enough to favor the phenomenon.

A further advance is due to Matthias,<sup>5</sup> who has proposed an empirical expression which applies generally to both the transition and nontransition metal superconductors where  $T_c$  is related to the atomic mass, the atomic volume and a function  $T(n)$  of the number of outer electrons. If a very rough proportionality between  $T_c$  and  $\gamma$  can be assumed to be generally applicable,  $T(n)$  may be regarded as a way of approximating the variation of the density of states function across the periodic table. Recently, Pines<sup>6</sup> has shown by use of a simple model how the Matthias regularities together with the theoretical prediction of  $T_c$  given in the BCS theory can produce a reasonable qualitative understanding of superconductivity in the nontransition metals. However, Pines' deductions concerning the transition metals are much less definite and suggest the need for a more thorough examination of this region of the periodic system both theoretically and experimentally.

In considering the above problems, we noted that previous experimental work was confined chiefly to individual element and compound superconductors with relatively little emphasis on the wide range of solid solution alloys that are available. It is true that a large number of superconducting alloy systems have previously been investigated,<sup>7</sup> but unfortunately most of these were based upon metals belonging to the "soft" group of superconductors such as tin, lead, and mercury. These elements exhibit a wide diversity of crystal structures and, moreover, they offer no single case in which a homogeneous solid solution of one structural type is formed over a complete range of binary alloy composition. In a few systems, such as lead-indium and lead-thallium, a single phase persists for more than 50% change in solute atom concentration, but in none of these cases does the composition change result in a large change of transition temperature. It is apparent, there-

<sup>1</sup> J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **106**, 162 (1957).

<sup>2</sup> J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

<sup>3</sup> J. G. Daunt, *Phys. Rev.* **80**, 911 (1950).

<sup>4</sup> H. W. Lewis, *Phys. Rev.* **101**, 939 (1956).

<sup>5</sup> B. T. Matthias, *Progress in Low Temperature Physics*, edited by J. C. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. 2.

<sup>6</sup> D. Pines, *Phys. Rev.* **109**, 280 (1958).

<sup>7</sup> D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1950), 2nd ed., p. 230.

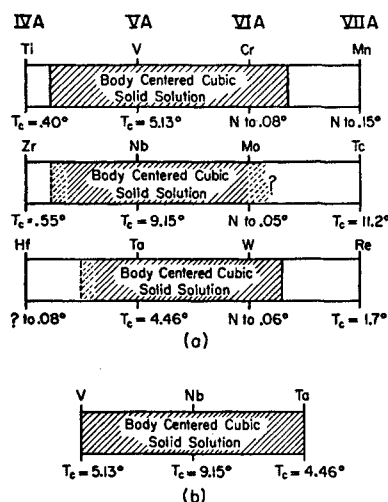


FIG. 1. Body-centered cubic solid solution ranges in the first three long periods.

fore, that the soft group of superconductors does not offer a representative case for a systematic study of the effect on the superconductive transition due to large changes of electronic structure.

However, if we consider the superconducting transition elements, we find a region approximately in the center of the transition metal group where the body-centered cubic crystal structure exists in solid solution over a wide range of composition between group 4 and group 7. At first sight, these metals, such as titanium, zirconium, vanadium, niobium, etc., seem rather unpromising for superconducting alloy studies owing to their non-ideal behavior under the influence of small amounts of impurity in particular dissolved gases.<sup>8</sup> In addition, their extremely high melting temperatures suggest possible metallurgical difficulties in preparing them. However, these disadvantages are greatly offset by the very wide range of solid solutions available. For example, consider the first long row elements, titanium, vanadium, and chromium. Both vanadium and chromium are body-centered cubic and form a body-centered cubic solid-solution over the entire range of binary alloy compositions.<sup>9</sup> Titanium, however, is hexagonal at room temperature but becomes body-centered cubic at high temperatures. Phase diagram studies have shown that the body-centered cubic phase can be retained by adding as much as 80 atomic percent of titanium to vanadium if proper cooling and annealing procedures are followed.<sup>10</sup> The series, titanium-vanadium-chromium, thus effectively permits a solute atom concentration change of more than 180% within a single phase region. Moreover, since vanadium and titanium are superconductors

and chromium is not, this alloy system offers the possibility of studying a complete transition from normal to superconducting behavior due to composition change within a single crystal structure.

The above discussion covers only the first long row elements, Ti-V-Cr. However, it is found that a wide range of solid solution of the body-centered cubic phase exists similarly for other transition metal alloy systems, in the second and third long periods, as shown in Fig. 1. It is immediately obvious that these systems offer a mechanism for varying the electronic configuration within a given crystal structure and should enable one to gain further insight into the role of the various mass, volume, and electronic structure effects in a superconductor.

In this paper, data are presented on the variation of the superconducting transition temperature with composition over the entire range of binary body-centered cubic solid solutions in the first three long periods. The most significant omission is the system molybdenum-technetium, for which a wide cubic region almost certainly exists in the neighborhood of pure molybdenum, with the possibility of a very high transition temperature due to the high value for technetium itself ( $11^\circ\text{K}$ ). Unfortunately, this system could not be studied due to the present unavailability of technetium. The system, chromium-manganese, also proved to be uninteresting from a superconducting viewpoint, presumably because of the onset of  $d$ -shell ferromagnetism in the first long period.

In the part of the periodic system upon which our attention is focussed, groups 4A to 7A, the existence of wide range solid solutions is, of course, not confined to individual rows but extends to various cross-combinations between rows which we have also studied. Superconducting data are presented for the "column" alloys, Ti-Zr-Hf and V-Nb-Ta, where one might expect the change of electronic configuration to be much less significant than in the case of row alloys. Data have also been obtained for various "diagonal" binary alloys cutting across both row and column. These systems are based chiefly on the metal, niobium, which occupies a "pivotal" role in the superconducting transition metal array.

It should be mentioned that two of the superconducting alloy systems described in this paper, Ti-V-Cr and Ti-Nb-W, were studied initially by one of the authors (J.K.H.) at the Institute for the Study of Metals, University of Chicago, in 1952. At that time, most of the starting materials were of rather low purity, so that only a rough survey of the superconducting situation was possible. Since 1952, considerable advances have been made in purifying the refractory transition metals, particularly those in group 5. Of particular importance to the present work was the availability of ultrapure zone-refined niobium made by Comenetz at Westinghouse Research Laboratories. As will be shown later, the superconducting results obtained on alloys prepared

<sup>8</sup> A. Wexler and W. S. Corak, Phys. Rev. **85**, 85 (1952).

<sup>9</sup> H. Martens and P. Duwez, Trans. Am. Soc. Metals **44**, 484 (1952).

<sup>10</sup> H. K. Adenstedt, J. R. Pequinot, and J. M. Raymer, Trans. Am. Soc. Metals **44**, 990 (1952).

from this material differ markedly from those obtained using the powdered niobium commonly available a few years ago, emphasizing the need for careful control of impurities in studies of the present type.

## II. EXPERIMENTAL DETAILS

### A. Superconducting Measurements

Superconducting transition temperatures were determined using an apparatus almost identical to the setup used for studies on transition metal compounds by Hardy and Hulm<sup>11</sup> (referred to hereafter as HH). The only modification of the HH technique was a refinement in thermometry. Formerly, a constant volume helium gas thermometer employing a mercury manometer for pressure measurement was used to obtain temperatures between 4.2° and 20°K. The mercury manometer required numerous time-consuming volume adjustments for each pressure reading. Therefore, in the present work, it was replaced by a dial pressure gauge specially constructed by the Wallace and Tiernan Company, Belleville, New Jersey, from their basic Precision Dial Manometer model FA145. With this gauge, it was possible to obtain gas thermometer pressures directly without the burdensome volume adjustment before each pressure measurement. Furthermore, after calibrating initially in the liquid helium range and applying suitable corrections for dead space volume, hydrostatic head, and deviations from ideal gas, temperatures between 4.2° and 20°K were known to be better than 0.01°K. Other standard gas thermometer corrections, such as thermomolecular pressure difference, external temperature difference, gravitation, absorption, etc., are effectively negligible and, therefore do not apply for this device.<sup>12</sup>

For measurements below 4.2°K, temperatures were determined from the vapor pressure of the liquid helium bath in which the samples were immersed using the T55E vapor pressure-temperature scale.<sup>13</sup>

The specimens were placed in a radial position about the gas thermometer bulb in the same manner as reported by HH. Fragmentary samples were enclosed in thin-walled, C-8 resin capsules upon which a detector coil of about 300 turns of 40-gauge insulated copper wire was wound. The smaller melted specimens were mounted in C-8 resin tubing which was cut away to allow the detector coil to be wound directly on the specimen. Each detector coil could be connected by switches to a high sensitivity ballistic galvanometer with a suitable damping resistance in series. The deflection of the galvanometer was observed when a measuring field of about five oersteds was applied or removed from the specimen. Entry of a specimen to the superconducting state was marked by a substantial

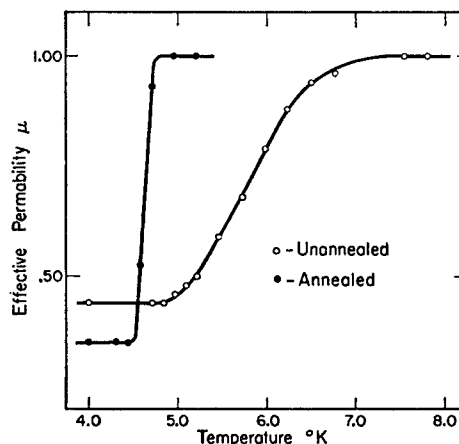


FIG. 2. Transition curves for Nb+10% Cr specimen before and after annealing.

decrease in this galvanometer deflection with decreasing temperature.

Transition curves for individual samples were obtained by plotting the temperature variation of the "effective permeability," a quantity obtained by dividing the galvanometer deflection at the measuring temperature by the deflection in the normal region (usually taken at liquid nitrogen temperatures). Typical transition curves in Fig. 2 show that entry to the superconducting state, as characterized by the effective permeability, sometimes takes place over a range of several degrees Kelvin. This effect is usually due to composition fluctuations and can, in most cases, be greatly reduced by suitable annealing treatment (Sec. II. D). However, even after annealing a residual breadth of about 0.1°K was typical for most of the alloys studied. Taking the transition temperature as the midpoint of the permeability curve, that is, the temperature at which the permeability is halfway between the completely normal and completely superconducting values, it seems reasonable to assume that for total transition breadths of 0.1°K the error in  $T_c$  due to composition fluctuations does not exceed a few hundredths of a degree.

The question of broadening due to the irregular shape of many of the samples and the finite measuring field was discussed fully by HH. Exactly the same considerations apply to the present work except that even smaller measuring fields were used. The field broadening calculated from HH, Eq. (2), does not exceed 0.001°K and, thus, can be ignored in comparison with inhomogeneity broadening.

For most of the specimens, the irregular shape made any attempt to make a superconducting critical field determination out of the question. However, a few samples were fabricated in cylindrical forms for which demagnetizing coefficients could readily be computed. In these cases, the change of total induction in the detector coil was determined as a function of the change of external field for fields up to about 1000 oe. In all

<sup>11</sup> G. F. Hardy and J. K. Hulm, Phys. Rev. **93**, 1004 (1954).

<sup>12</sup> J. K. Hulm and R. D. Blaugher, Cryogenics **1**, 229 (1961).

<sup>13</sup> J. R. Clement, Naval Research Laboratory, Washington, D. C. (unpublished).

TABLE I. Characteristics of the samples.

Metal	Form	Gaseous impurities		Major metallic impurities (ppm)	Source and designation
		O <sub>2</sub>	N <sub>2</sub>		
Nb	Zone-refined rod	100	180	Ta < 1440; Zr < 400; C < 100	Westinghouse CZ-3
Nb	Sintered	490	110	Ta < 1500; C < 220; Fe, Si, Ti < 300	Electromelt (EM-5)
Hf	Bar	35	10	Fe < 1000; Zr < 500	Westinghouse reactor grade
W	Rod	10	<i>nd</i>	Fe, Si, Mo < 30	Westinghouse S-grade
Mo	Sheet	<sup>a</sup>		Ni < 100; Al, Fe, Si, Mg, Mn, Si, V < 70	Westinghouse
Re	Powder	<sup>a</sup>		No majors in detectable amounts	University of Tennessee
Ta	Electron-beam-melted sheet	<sup>a</sup>		U < 400; Mo < 300; Ag < 135; Nb < 130	Electromelt
Ti	Iodide bar	<sup>a</sup>		Sb, As < 1000; Fe < 100	Battelle Memorial Institute
Zr	Sponge	<sup>a</sup>		Hf < 910; Fe < 360; Cr < 63	Carborundum
Zr	Bar	<sup>a</sup>		Hf < 20, 500; Si < 220; Fe < 62	Westinghouse A-3057
V	Iodide bar	<sup>a</sup>	<sup>b</sup>	Fe < 280; Nb, Ti < 400; Zr < 100	Battelle Memorial Institute
Cr	Bar	<sup>a</sup>		Fe < 1140; Al < 20; Mo < 640; Rb, Nb < 800; Se < 350; Na < 140	1939 Chevrolet

<sup>a</sup> Gaseous impurities were not determined.<sup>b</sup> Vickers hardness 45 dph.

cases, the destruction of superconductivity took place very gradually over a wide range of field and was incomplete at the highest field. The determination of a reliable critical field value from such curves proved to be impossible.

### B. Starting Materials

Extensive literature now exists on the influence of impurities on the superconducting behavior of the transition metals.<sup>8,14</sup> Much of this work constitutes an inquiring into the causes of the very broad transitions which are frequently found to accompany the destruction of superconductivity by a magnetic field, particularly for vanadium, niobium, and tantalum. The chief culprit appears to be dissolved gas, either nitrogen or oxygen, which produces very broad magnetic field transitions unless the gas content is maintained at a level considerably below 100 parts per million (ppm). Despite recent advances in zone refining and electron bombardment melting, gas contents lower than 100 ppm are still difficult to achieve in the transition elements and are even more impracticable for transition metal alloys, which, in addition, have to be homogenized with respect to their metallic constituents.

In the present work, no serious attempt was made to achieve alloys with gas contents low enough to yield sharp magnetic transitions. Our main interest was the variation of  $T_c$  with metallic composition. In deriving  $T_c$  from various effective permeability-temperature curves, as described in the previous section, it was found that the shape and location of these curves was much less sensitive to gaseous impurities than were the isothermal magnetic field transitions. It was observed that  $T_c$  was not appreciably affected until gas contents in the vicinity of 1000 ppm or more were attained. Thus, gaseous impurities at the 100 ppm level were considered tolerable in our experiments, and as Table I indicates,

this level was typical for most of the starting metals used.

Of particular importance to the present study was the availability of generous quantities of ultrapure niobium supplied by Begley using a special zone-refining process.<sup>15,16</sup> To illustrate the effect of excessive gas content, the transition temperatures of various niobium-tungsten alloys prepared using zone-refined niobium are compared in Fig. 3 with  $T_c$  for an earlier series of samples prepared from powdered niobium. It should be remarked that the straight line for the zone-refined material was based upon data beyond 15% tungsten content, as well as on the experimental points shown in Fig. 3. The powdered metal had a gas content in the neighborhood of 3000 ppm, which apparently shifted  $T_c$  downwards by 3°K or more. Attempts were made to reduce this shift by annealing the samples in vacuum, but  $T_c$  remained steady, even though the effective permeability versus temperature curve was considerably sharpened.

So far, little reference has been made to metallic impurities, mainly because these are believed to be of minor importance at the levels encountered in Table I materials. There is little doubt that different metallic impurities differ greatly in their effectiveness in shifting  $T_c$ .<sup>5</sup> For example, in group 5 the most depressive effect appears to result from group 8 impurities, particularly from the ferromagnetic elements. However, this effect is not serious provided that the group 8 impurity content is held well below 1000 ppm.

### C. Melting Techniques

The majority of specimens were melted in an arc furnace on a water-cooled copper hearth using a tungsten electrode. Spectroscopic analysis of a representative number of specimens showed this technique produced no copper or tungsten contamination in the melt from

<sup>15</sup> R. T. Begley, Wright Air Development Center Report TR 57-344, 1957 (unpublished), part I (1957), p. 89.

<sup>16</sup> R. T. Begley, reference 15, part II (1958), p. 143.

<sup>14</sup> J. K. Hulm and B. B. Goodman, Phys. Rev. **106**, 659 (1957).

the hearth and electrode, respectively. Since the tungsten arc furnace could not be operated in a high vacuum, melting had to be done in a pure, inert atmosphere with a pressure of about 30 to 100 mm Hg. A reasonably pure atmosphere was obtained by evacuating and purging the furnace chamber several times with argon. Finally, a zirconium button was melted in order to further purify the atmosphere and to reduce the possibility of gas contamination in the remaining melts. Usually three specimens and the zirconium button were placed in the furnace chamber. After the initial melt, without opening the furnace, the buttons were turned and remelted several times to ensure complete mixing. However, by virtue of the rapid quenching characteristic of the arc furnace, a small grained inhomogeneous specimen of mixed composition and variable physical parameters was usually produced. This necessitated vacuum annealing treatment for many of the specimens, as described in Sec. II. D.

Some specimens could not be homogenized by arc melting and vacuum annealing, while others vaporized excessively or experienced preferential separation by this method. For these particular specimens, it was necessary to use an alternate technique known as levitation melting<sup>17,18</sup> for the preparation. Levitation melting enables one to obtain a homogenized specimen readily by virtue of its vigorous electromagnetic stirring action, and since the temperature can be controlled accurately, it is possible to operate close to the melting point of the specimen, thus decreasing any vaporization. The levitation melted specimens were approximately cylindrical with rounded ends resembling somewhat the familiar button shape obtained in arc-melting small samples.

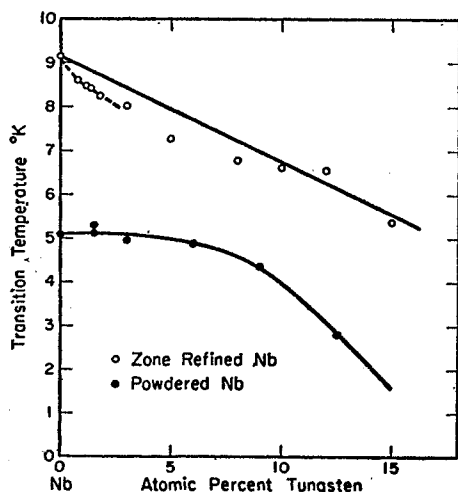


FIG. 3. Transition temperatures versus composition for niobium-tungsten alloys prepared from different starting materials.

<sup>17</sup> D. M. Wroughton, E. L. Okress, P. H. Brace, G. Comenetz, and J. C. R. Kelly, *J. Appl. Phys.* **23**, 545 (1952).

<sup>18</sup> D. M. Wroughton, E. L. Okress, P. H. Brace, G. Comenetz, and J. C. R. Kelly, *J. Electrochem. Soc.* **99**, 205 (1956).

TABLE II. Sources of the alloy samples.

Alloy system	Source
Ti-V	H. K. Adenstedt, J. R. Pequignot, and J. M. Raymer, USAF Wright-Patterson Materials Laboratory
V-Cr	P. Duwez and H. Martens, California Institute of Technology
Nb-Hf, Nb-Mo, Nb-Zr	R. T. Begley, Westinghouse Research Laboratories
W-Re, Ta-W, Ta-Hf	L. L. France and L. S. Richardson, Westinghouse Research Laboratories
Ti-Nb	M. Hansen, E. L. Kamen, H. D. Kessler, and D. J. McPherson, Illinois Institute of Technology
Ta-W, Ta-Hf	A. R. Kaufman, Massachusetts Institute of Technology

Additional samples of a number of the systems of interest were obtained through the kind cooperation of workers in our own and other laboratories. These particular samples and their source are listed in Table II. The preparation of these samples were essentially identical with our own previously discussed techniques. Some samples, however, required annealing in order for them to be similar in heat treatment to our specimens.

#### D. Annealing and Quenching

Due to the difficulty of maintaining ultra-high vacuum conditions at temperatures above 1500°C for long periods, long-time annealing treatment tends to increase the gas content of transition elements. Therefore, we sought ways to avoid this treatment in our preliminary investigations and studied the superconducting behavior of unannealed arc-melted samples. Figure 2 shows a typical transition curve for this type of sample in the niobium-chromium system. The onset of superconductivity occurs over a range of about 2°K, and it is fairly evident that the value of  $T_c$  obtained from such a curve could not be very reliable. Metallographic examination of the sample showed a heterogeneous grain structure with fine crystallites which appeared to be highly strained [Fig. 4(a)].

Since most of the directly melted samples gave unsatisfactory transition curves, we had to resort to annealing treatment with the resulting risk of gas contamination. Most of our anneals were made in the induction furnace at temperatures between 1500° and 2500°C, depending on the melting point of the particular specimens. Annealing periods of between 50 and 100 hr were employed with an average furnace pressure of  $3 \times 10^{-6}$  mm of mercury. The effect of such treatment on our typical niobium-chromium sample at 2200°C was quite dramatic, as shown in Fig. 2. The transition curve not only sharpened markedly, but its center was displaced downward by about 1°K. The metallograph [Fig. 4(b)] showed considerable grain growth and disappearance of the highly-strained condition. It is im-

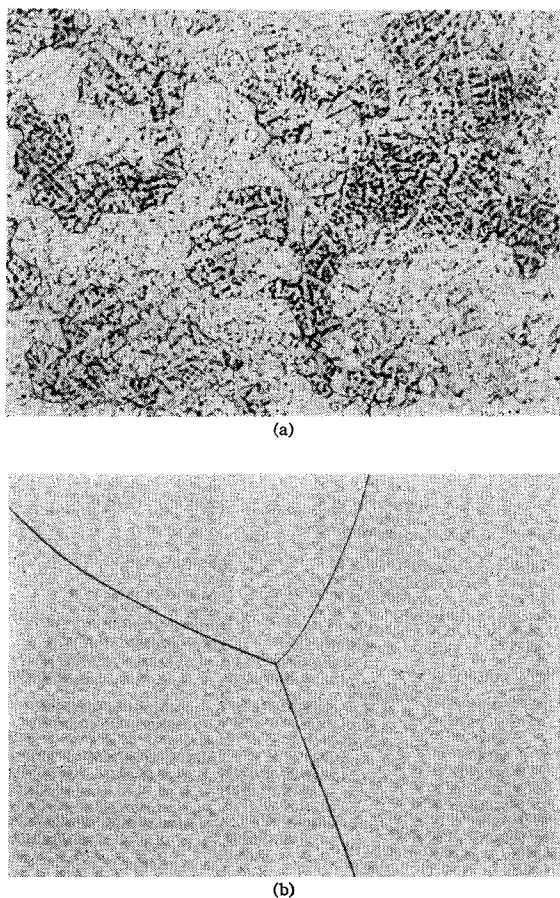


FIG. 4. Metallograph for Nb+10% Cr specimen before and after annealing.

portant to remark that vacuum fusion analysis performed both before and after annealing showed very little change in gas content, evidence of satisfactory vacuum conditions in our furnace.

When chromium is dissolved in niobium,  $T_c$  is depressed. Thus, the lowering of  $T_c$  caused by annealing the Nb plus 10% Cr sample suggests that in the as-melted sample there existed regions of enriched chromium surrounded by regions of depleted chromium. To explain the observed superconducting behavior, we may assume that the dilute chromium regions become superconducting at a higher temperature than the true transition temperature for the homogeneous sample and, moreover, that they shield the regions of higher chromium content in such a way that the apparent volume of superconducting material is greater than the actual volume of superconducting material within the sample. That this shielding effect is incomplete may be deduced from the fact that the limiting effective permeability as  $T$  approaches zero for the un-annealed sample is appreciably greater than that for the annealed sample (see Fig. 2).

Frequently, the only effect of annealing was to reduce

the breadth of the transition curve without displacing its center point appreciably. As might be expected, this was usually the case in regions where the transition temperature was found to be rather insensitive to composition changes.

In the annealing procedure so far described, little effort was made to reduce the temperature quickly at the end of the heating cycle. The induction heater was simply switched off and the sample was allowed to cool at a slow rate determined usually by the heat capacity of a large susceptor and mount of molybdenum. This procedure was adequate for most of the specimens, particularly for those with compositions well removed from the limits of the body-centered cubic range. Close to these limits, however, we encountered difficulties which required a setup for rapid quenching of specimens at the end of the annealing time.

The quench technique was required mainly in connection with the so-called "martensite" transformation exhibited by several of the binary systems formed between group 4 and group 5 metals. This transformation occurs in the vicinity of the lower limit of existence of the body-centered-cubic phase with respect to valence number, usually around 4.2 valence electrons per atom. Since it was desired to extend the superconducting data for the cubic phase down to the lowest possible valence number, the superconducting effects of the martensite transformation were studied in detail for the typical systems, Ti-V and Ti-Nb. Martensite transformations are also known to occur in several other binary systems of interest in our work, for example, Zr-Nb, Hf-Ta, and Hf-Nb. However, since detailed phase diagram data is lacking for these systems, their superconductivity was not studied in the transformation region.

In the martensite region, the systems Ti-Nb and Ti-V resemble each other closely with respect to phase constitution, transformation kinetics, and superconducting behavior. Thus, only the results for Ti-Nb need be discussed in detail. Figure 5 shows the relevant portion

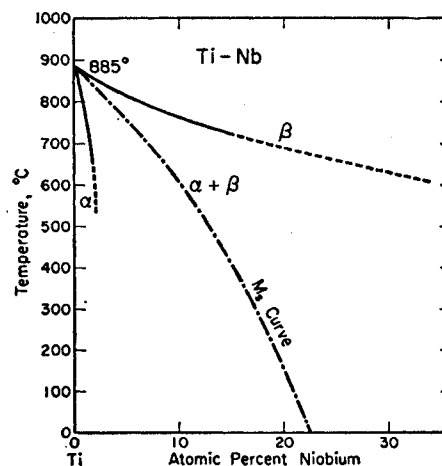


FIG. 5. Part of titanium-niobium phase diagram.

of the Ti-Nb phase diagram according to Hansen *et al.*<sup>19</sup> To this diagram, we have added the martensite transformation curve ( $M_s$  curve) due to Duwez.<sup>20</sup> The  $M_s$  curve represents the point at which, with decreasing temperature, some of the high-temperature cubic or  $\beta$  phase undergoes a diffusionless transformation to a hexagonal  $\alpha'$  phase with the same composition as the parent material. Kaufman<sup>21</sup> believes that on the basis of thermodynamic data, Fig. 5 is inaccurate. However, a refinement of the diagram would not affect its qualitative features, which are thought to be sufficiently reliable for the present discussion.

Figure 5 indicates that an alloy cooled from the high temperature cubic region might break up into three distinct types of material. As the upper ( $\alpha+\beta$ ,  $\beta$ ) phase boundary is crossed, hexagonal  $\alpha$  material might be formed of composition determined by the ( $\alpha$ ,  $\alpha+\beta$ ) phase boundary. This would cause a niobium enrichment of the remaining cubic  $\beta$  material, probably in a highly inhomogeneous fashion owing to low rates of diffusion. Further cooling down to the  $M_s$  curve could result in a martensite precipitation of  $\alpha'$  hexagonal with the same composition as the parent  $\beta$ . However, inhomogeneities in  $\beta$  could cause similar inhomogeneities in  $\alpha'$ . The final alloy might consist, in general, of  $\beta$ ,  $\alpha$ , and  $\alpha'$  with a considerable composition spread.

The actual yield of  $\beta$ ,  $\alpha$ , and  $\alpha'$  material is determined chiefly by the starting composition and the rate of cooling. For niobium contents greater than about 50 atom percent, the  $\beta$  phase is retained irrespective of cooling rate, probably because  $\alpha$  precipitation is too sluggish to occur in the low-temperature region obtained by extrapolating the ( $\alpha+\beta$ ,  $\beta$ ) boundary line. From 50% down to 20% niobium, this sluggish  $\alpha$  reaction can still be inhibited by water quenching directly from the  $\beta$  region. However, slow cooling results in an  $\alpha$  precipitate which increases in amount as the starting niobium content is decreased.

The superconducting data for water quenched samples is compared in Fig. 6 with transition temperatures for samples slow cooled in the induction furnace. In the region of 20 to 50 atomic percent niobium, the data are quite consistent with the above reaction picture. The quenched samples gave relatively sharp single transitions, presumably characteristic of pure  $\beta$  material. The slow-cooled samples gave spread-out transitions, often consisting of two or more distinct regions of decreasing permeability. In these samples, the  $\alpha$  phase is thought to be nonsuperconducting above 1°K (data for pure  $\alpha$  samples suggest this). However, as the  $\alpha$  phase precipitates, the remaining  $\beta$  material grows richer in niobium content, which explains not only the spread-

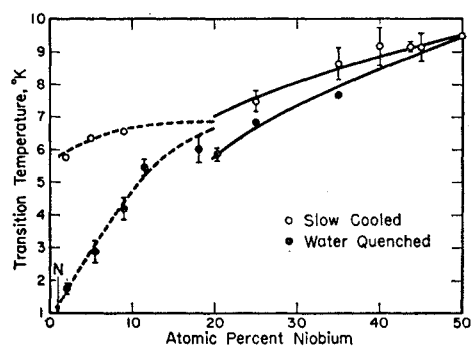


Fig. 6. Transition temperature versus composition for titanium-niobium alloys prepared by different types of heat treatment.

out transitions for these samples, but also the higher value of  $T_c$  relative to the pure  $\beta$  curve.

Since the extrapolated  $M_s$  curve goes below room temperature at about 22 atom percent niobium, some concern was felt that samples of the pure type obtained by quenching to room temperature in the 20 to 50% niobium range might undergo a martensite reaction when cooled to liquid helium temperatures for superconducting measurements. According to the work of Kurdjumov,<sup>22</sup> the possibility of a martensite reaction occurring below room temperature would be materially decreased by further quenching to liquid nitrogen or liquid helium temperatures, which was invariably done in our work. Furthermore, the occurrence of sharp, single superconducting transitions is good evidence that no  $\alpha'$  was generated. In resistivity measurements on very similar samples, Ames and McQuillan<sup>23</sup> found no evidence of resistive anomalies such as might be expected in the vicinity of a low temperature transformation. We are, therefore, confident that a martensite reaction below room temperature can be ruled out in the present work.

For niobium contents below about 20 atom percent, it is likely that both  $\alpha$  and  $\alpha'$  precipitates are formed. In this range, we were surprised to find that whereas quenched samples exhibited spread-out superconducting transitions, the slow-cooled samples gave quite sharp, single transitions. This behavior is an exact reversal of that found above 20% niobium.

Considering first the quenched samples, all evidence points to the formation of an  $\alpha'$  phase of composition close to nominal. Probably the production of  $\alpha$  is inhibited by quenching, but not entirely suppressed. Hence, some spread of composition of the resulting  $\alpha'$  precipitate is to be expected, and this is borne out by the broadening of superconducting transitions. The niobium content of the  $\alpha'$  should nevertheless be fairly close to the initial or nominal content, and the variation of superconducting transition temperature with niobium content is perfectly consistent with this assumption.  $T_c$  decreases with decreasing niobium content, and the

<sup>19</sup> M. Hansen, E. L. Kamen, H. D. Kessler, and D. J. McPherson, *Trans. Am. Inst. Mining, Met. Petrol. Engrs.* **191**, 881 (1951).

<sup>20</sup> P. Duwez, *Trans. Am. Soc. Metals* **45**, 934 (1953).

<sup>21</sup> L. Kaufman, *Acta Met.* **7**, 575 (1959).

<sup>22</sup> G. V. Kurdjumov, *J. Metals* **10**, 449 (1959).

<sup>23</sup> S. L. Ames and A. D. McQuillan, *Acta Met.* **2**, 831 (1954).

curve extrapolates to about  $0.5^\circ\text{K}$  for zero niobium, in good agreement with the value of  $0.49^\circ\text{K}$  reported for pure titanium.<sup>24</sup>

The sharp, superconducting transitions observed for the slow-cooled samples are also understandable if one assumes that in this case a nonsuperconducting  $\alpha$  precipitate is formed with cooling, causing steady niobium enrichment of  $\beta$  with decreasing temperature. The composition follows the full  $(\alpha+\beta, \beta)$  curve down to the beginning of the dotted region, at which point  $\alpha$  precipitation essentially ceases and the sample follows a constant composition path down through the  $M_s$  curve. The resulting sample is an  $\alpha'$  precipitate of practically constant niobium content (between 15 and 20%), independent of the initial content. Consequently,  $T_c$  lies in the vicinity of  $6^\circ\text{K}$  and is practically independent of starting niobium concentration.

### III. RESULTS AND DISCUSSION

#### A. Binary Alloys of Neighboring Row Elements

The superconducting transition temperatures of binary alloys formed between neighboring group 4, 5, and 6 elements and one group 7 element in the first three long periods are plotted against composition in Figs. 7, 8, and 9, respectively. Some compositions which remained normal down to about  $1^\circ\text{K}$  are shown by vertical arrows with the letter  $N$  above. In the region of the martensite transformation, we have shown only data for the pure cubic phase to the limit of its existence and beyond this a dotted curve for the pure hexagonal phase. While this paper was being prepared, results on the Ti-V-Cr system were published by Muller.<sup>25</sup> His data are in general agreement with the present work.

A number of striking features of superconducting behavior are common to the row alloys of the three long periods. The following points are considered significant.

(1) There are two distinct maxima of transition temperature, one located between group 4 and group 5 close to the valence number 4.7, and the second located between group 6 and group 7 close to the valence number 6.4.

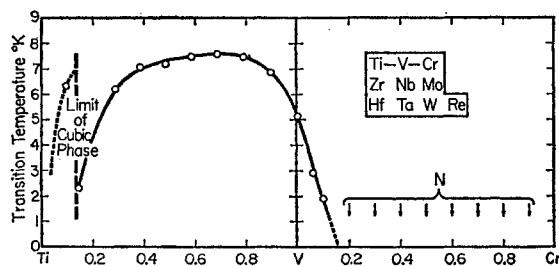


FIG. 7. Transition temperature versus composition for Ti-V-Cr.

<sup>24</sup> M. C. Steele and R. A. Hein, Phys. Rev. **92**, 243 (1953).

<sup>25</sup> J. Muller, Helv. Phys. Acta. **32**, 141 (1959).

(2) There is no discontinuity of slope at the group 5 element, that is,  $\partial T_c/\partial c$  has equal values of opposite sign due to the addition of group 4 and group 6 elements, respectively, provided these are in the same row.

(3) The transition temperature of each group 5 element is depressed in a linear fashion by the addition of each group 6 element.

We may immediately conclude that there is general agreement between the present results and the point of view expressed by Matthias.<sup>5</sup> In fact, we may regard the curves of Fig. 7-9 as a more accurate representation of the  $T(n)$  function of Matthias, where, as was pointed out in our introduction,  $T(n)$  is probably a rough approximation to the density of states at the Fermi surface. The positions of the maxima, 4.7 and 6.4, are substantially different from the values of 5 and 7 va-

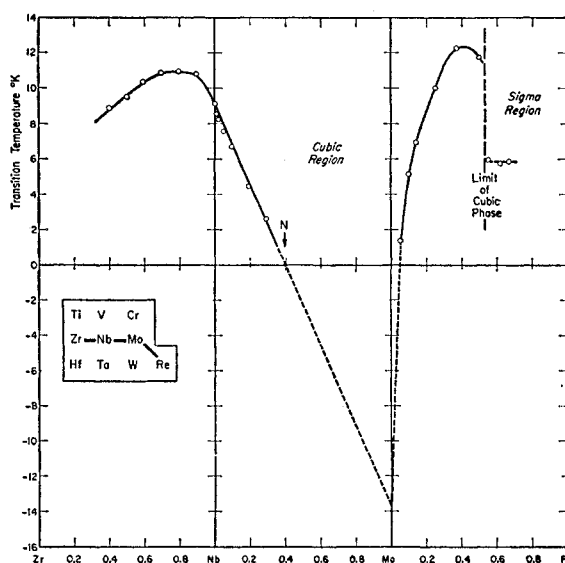


FIG. 8. Transition temperature versus composition for Zr-Nb-Mo-Re.

lence electrons per atom originally proposed by Matthias. However, Matthias has indicated that his original figures were approximate ones, based chiefly upon the behavior of the individual elements. The present alloy data for the upper maximum are in excellent agreement with results for uranium compounds obtained by Chandrasekhar and Hulm<sup>26</sup> and intermetallic compound data obtained by Blaugher and Hulm.<sup>27</sup>

Consider the second point of significance, the continuity of slope of the transition temperature versus composition curve on passing through any of the group 5 elements along the same row. One is tempted to explain this effect as a movement of the Fermi level along a continuous density-of-states curve. The validity of

<sup>26</sup> B. S. Chandrasekhar and J. K. Hulm, J. Phys. Chem. Solids **1**, 259 (1958).

<sup>27</sup> R. D. Blaugher and J. K. Hulm, J. Phys. Chem. Solids **19**, 134 (1961).

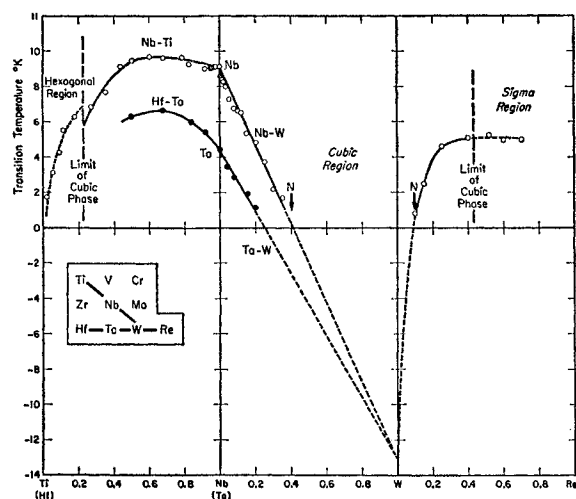


FIG. 9. Transition temperature versus composition for Ti-Nb-W-Re, Hf-Ta-W-Re.

this viewpoint rests upon the assumption that the density of states curve is little influenced by the addition of a solid solution impurity of mass only slightly different from the solvent atom. This seems like a reasonable assumption for small impurity contents, say, up to a few percent, which is the range over which our data indicate a continuous slope.

The previous considerations have led us to a more general assumption which, if it is true, would appear to contain an explanation of many of the electronic properties of the transition metals and their alloys. We assume that the  $T(n)$  curve, presumably in its more accurate form as represented by Figs. 7-9, represents a general shape of the  $d$  band common to the majority of the transition elements. We are transposing, of course, from a plot of  $T_c$  versus average number of valence electrons to a plot of density of states versus energy. In addition to the maxima at 4.7 and 6.4 electrons per atom, we presume the existence of two other maxima at approximately 3 and 9 electrons per atom, respectively. The evidence for the last two maxima is provided chiefly by the normal electronic properties,<sup>28</sup> although for reasons which are not yet understood, there seems to be no maximum of superconducting transition temperature in the vicinity of 9 electrons per atom. Assuming, then, that there is a universal  $d$ -band shape containing four distinct maxima, we may expect this shape to be maintained in any process of alloy or compound formation between the transition elements. The electronic properties of the resultant material will be determined chiefly by settling of the Fermi level at some intermediate position on the universal  $d$ -band curve.

The above picture is certainly an oversimplification of the transition element band structure, particularly since it fails to account for the absence of superconduc-

tivity in the vicinity of 9 valence electrons per atom. Nevertheless, the picture does provide a rather satisfactory means of tying together most of the alloy data in the present paper. It further explains the correlation between  $T_c$  and valence number for transition metal compounds in which the individual constituents belong to widely separated groups.<sup>5</sup>

The last point to be discussed is the linear dependence of  $T_c$  upon concentration for the group 5-group 6 solid solutions. This is particularly marked in Figs. 8 and 9 where the straight lines have been extrapolated to intersect the group 6 ordinate. In Fig. 9, this extrapolation was also performed for the diagonal system Nb-W. We were greatly surprised when both the Ta-W and the Nb-W lines intersected quite accurately at the same negative temperature on the group 6 ordinate. This remarkable result led us to the concept of assigning negative transition temperatures to the first three body-centered-cubic group 6 elements as follows:

chromium,	$T_c = -35^\circ\text{K}$ ;
molybdenum,	$T_c = -13.6^\circ\text{K}$ ;
tungsten,	$T_c = -13.0^\circ\text{K}$ ;
uranium,	$T_c = +1.8^\circ\text{K}$ .

For chromium and tungsten, a pair of extrapolations were performed in each case, with the identical result for each metal. Only five of the possible nine binary combinations between group 5 and group 6 were actually studied by us, and a further test of the negative  $T_c$  concept will be possible when data on the other four combinations become available. The transition temperature for body-centered-cubic uranium is taken from the work of Chandrasekhar and Hulm,<sup>26</sup> who extrapolated data on uranium-niobium and uranium-molybdenum alloys to 100% uranium. It is interesting that  $T_c$  increases monotonically as one descends group 6.

In contrast to the linear behavior of  $T_c$  between group 5 and group 6, we observed a very steep, non-linear behavior between group 6 and group 7. In the case of the Re-Mo and Re-W alloys, it is possible to draw a reasonable extrapolation down to the postulated negative transition points for Mo and W, respectively, but one cannot help noticing the marked asymmetry of the minimum in  $T_c$ . It is possible that our straight-line extrapolations below 1°K should be replaced by a more rounded plot with a gradual minimum between group 5 and group 6. The verdict on this point will probably have to wait upon a careful determination of the electronic heat capacity in the range of interesting compositions, plus a better understanding of the relationship between  $T_c$  and  $\gamma$ .

## B. Binary Alloys of Diagonal Neighbors

Only two diagonal alloy systems were examined in detail, both centered on the element niobium. The superconducting transition temperatures are plotted as

<sup>28</sup> D. H. Parkinson, *Reports on Progress in Physics* (The Physical Society, London, 1958), Vol. 21.

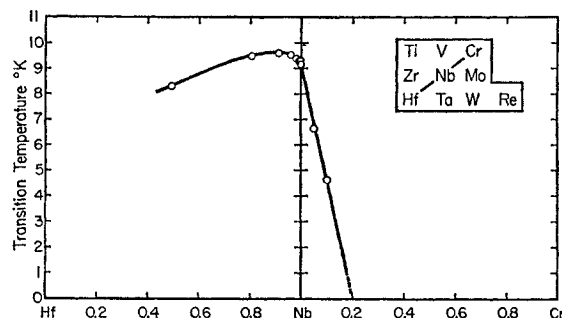


FIG. 10. Transition temperature versus composition for Hf-Nb-Cr.

a function of composition in Figs. 9 and 10 for the systems, Ti-Nb-W and Hf-Nb-Cr, respectively. The martensite transformation in Ti-Nb alloys has already been discussed, and the data shown are only those for the pure cubic and pure hexagonal phases.

The general form of both of the diagonal transition temperature curves is very similar to that for the row alloys, with a pronounced maximum between group 5 and group 6. We must point out, however, that the maxima are displaced somewhat from the vicinity of 4.7 valence electrons per atom, the value which is typical for the row alloys. The greatest displacement occurs for the Hf-Nb system where the maximum lies between 4.9 and 5.0 valence electrons per atom. At present, we have no explanation of this effect.

A second feature which distinguishes the diagonal alloys from the row alloys is a break in slope as the group 5 element, niobium, is traversed. This break is very much apparent for the Ti-Nb-W system (Fig. 9). It is not so obvious in the Hf-Nb-Cr system (Fig. 10) owing to the rapid change of slope on the hafnium side close to pure niobium.

One major point of difference between the diagonal alloys and the row alloys is that the difference in mass between the solute and solvent atoms is much larger in the diagonal case than in the row case. While this large mass difference may, perhaps, be responsible for the discontinuity in slope at group 5, it is easy to show that the observed change of slope (which amounts to about 20°K per valence electron) is an order of magnitude larger than that calculated for the actual masses of titanium, niobium, and tungsten using the isotope expression

$$M^{\frac{1}{3}}T_c = \text{constant.} \quad (1)$$

We are, therefore, inclined to view the slope change as primarily electronic in origin. In terms of the "universal  $d$ -band" picture discussed in the previous section, these results seem to indicate that only the general shape of the band is preserved on passing from row to row, while the actual magnitude and slope of the density of states curve change radically. With our present ignorance on the relationship of  $T_c$  and  $\gamma$ , it is not pos-

sible to make quantitative statements regarding these changes.

### C. Binary Alloys of Neighbors in Columns

The final experiments were concerned with alloys of neighboring transition elements in the 4th and 5th columns. The cubic alloys in the 6th column were not investigated owing to the high negative transition temperatures discussed previously for Cr, Mo, and W. The 7th column could not be studied adequately due to the present unavailability of technetium.

The superconducting transition temperatures for alloys in groups 4 and 5 are plotted against vertical composition in Figs. 11 and 12, respectively. The vertical arrows with the letter  $N$  above represent temperatures down to which normal behavior was observed for the composition so denoted.

All samples of group 4 alloys were of the hexagonal close-packed structure. The Ti-Zr alloys showed a well-defined transition temperature maximum in the midpoint of the range. Data in the Zr-Hf series are incomplete due to the very low transition temperatures encountered in this region. Three compositions in the latter series were studied down to 0.35°K, using a helium-3 cryostat, but no trace of superconductivity could be found. The dotted curve is, therefore, a speculative one based upon our normal data and the range of transition temperatures reported by others<sup>29-31</sup> for hafnium metal.

In group 5, difficulties were encountered in attaining reasonably sharp superconducting transitions for alloys of the V-Nb series at the niobium rich end, despite prolonged annealing. Data based upon some very broad transitions found between 80 and 100% Nb have been omitted, but this does not affect the general form of the transition temperature versus composition curve.

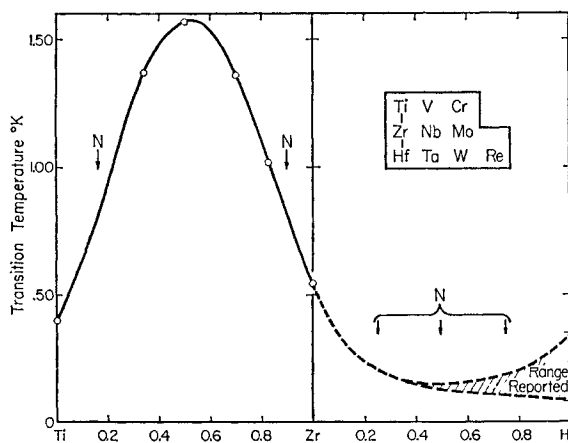


FIG. 11. Transition temperature versus composition for Ti-Zr-Hf.

<sup>29</sup> L. D. Roberts and J. W. T. Dabbs, Phys. Rev. **86**, 622 (1952).

<sup>30</sup> T. S. Smith and J. G. Daunt, Phys. Rev. **88**, 1172 (1952).

<sup>31</sup> R. A. Hein, Phys. Rev. **102**, 1511 (1956).

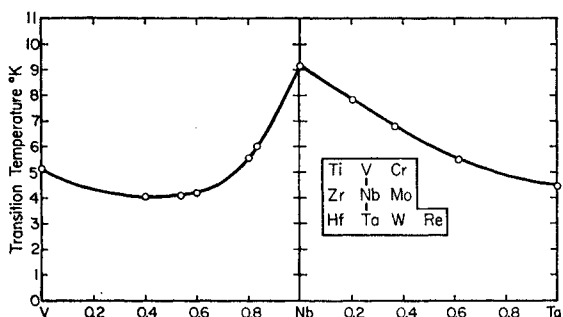


FIG. 12. Transition temperature versus composition for V-Nb-Ta.

It is very hard to explain this apparent metallurgical difficulty, since no phase transition or other anomalies are reported in the critical region. Calverley and Rose-Ines<sup>32</sup> have recently given data on electron bombardment-melted specimens in the Nb-Ta series. Their transition temperature versus composition curve is in excellent agreement with our results for Nb-Ta in Fig. 12.

Comparing the general form of the curves in Figs. 11 and 12, one observes that even allowing for the speculative form of the Zr-Hf region, there is a marked difference in behavior between group 4 and group 5 alloys. From arguments concerning the transition temperatures of the individual elements in both these groups, Matthias<sup>5</sup> has proposed a dependence on mass  $M$  and volume  $V$  of the form

$$T_c \sim V^x/M, \quad (2)$$

where  $x$  lies between 4 and 5. This empirical expression does not come close to fitting the alloy data in Figs. 11 and 12. Even if one is permitted to use arbitrary exponents for  $V$  and  $M$ , an expression of this type is incapable of accounting for the minimum in the V-Nb system and the probable negative  $T_c$  value for pure hafnium. The difficulty probably stems from neglect of the density of states contribution in expression (2). Changes of  $\gamma$  on passing down a given group could easily mask the volume and mass effects. However, further data on  $\gamma$  are required before this question can be attacked quantitatively.

### CONCLUSION

Our studies of the superconducting transition temperatures of solid solution alloys of the transition metals permit us to conclude that as one moves along a given row of the periodic table, the transition temperature shows at least two distinct maxima. The location of these maxima correspond approximately to similar peaks in the density of states function,  $N(0)$  (at the Fermi surface); although for the alloys in question, the  $N(0)$  data are indirect and incomplete. A connection of

some type between  $T_c$  and  $N(0)$  is certainly consistent with current theories of superconductivity. For example, Bardeen, *et al.*<sup>1,2</sup> predict

$$kT_c = 1.14 \langle \hbar\omega \rangle_{av} \exp\{-1/N(0)V\}, \quad (3)$$

where  $\langle \hbar\omega \rangle_{av}$  is the mean energy of phonons which scatter electrons at the Fermi surface, and  $V$  is an interaction parameter between electrons which causes superconductivity.

Pines<sup>6</sup> and Suhl *et al.*<sup>33</sup> have discussed the application of the BCS theory to various types of band structure. Pines suggests that for the transition metals which have a narrow  $d$  band with a high density of states, one might expect a decoupling of  $V$  and  $N(0)$  with a fairly constant value of the interaction parameter. Goodman *et al.*<sup>34</sup> have applied Eq. (3) to certain uranium alloys and from experimental values of  $T_c$  and the heat capacity have calculated the parameter  $V$  as a function of composition. They conclude that  $V$  is indeed insensitive to changes in composition, in agreement with Pines's prediction.

If, following Goodman *et al.*,<sup>34</sup> we substitute  $\frac{3}{4}k\Theta$  for  $\langle \hbar\omega \rangle_{av}$ , where  $\Theta$  is the Debye temperature, Eq. (3) becomes

$$T_c/\Theta = 0.855 \exp\{-1/N(0)V\}. \quad (4)$$

Since the left-hand side of Eq. (4) lies in the vicinity of 0.01 for the uranium alloys referred to above, the coefficient of the exponential is rather insensitive to changes in  $T_c$ . Indeed, a decrease of  $T_c$  by a factor of 10 will only produce about 50% change in  $N(0)V$ . Since the actual change of  $T_c$  for the uranium alloys was only about 10% over the full range of composition, the expected change of  $V$  from Eq. (4) would be extremely small. We, therefore, suspect that the test of the theory applied by Goodman *et al.*<sup>34</sup> is not very conclusive.

We are hampered by the lack of  $N(0)$  data in applying Eq. (4) to the alloys of the present work. However, some very approximate heat capacity data for the Ti-V-Cr system have recently been published by Cheng *et al.*<sup>35</sup> In order to apply the theory, we have accepted the Pines assumption that  $V$  is approximately constant, and we have used Eq. (4) to calculate  $V$ , or more precisely  $N(0)V/\gamma$ , where  $\gamma$  is the coefficient of the electronic heat capacity, for pure vanadium. This value of  $N(0)V/\gamma$ , 26.7 deg<sup>2</sup> mole joule<sup>-1</sup>, is then used to convert the experimental  $\gamma$  values in the second column of Table III to  $N(0)V$  values in the third column. Substituting  $N(0)V$  and  $\Theta$  in Eq. (4), we have calculated  $T_c$  for the Ti-V and V-Cr alloys.

The calculated  $T_c$  values for the Ti-V and V-Cr systems are compared with the actual measured values

<sup>33</sup> H. Suhl, B. T. Matthias, and L. R. Walker, *Phys. Rev. Letters* **3**, 552 (1959).

<sup>34</sup> B. B. Goodman, J. Hillairet, J. J. Veyssie, and L. Weil, *Proceedings of the Seventh International Conference on Low-Temperature Physics, 1960* (University of Toronto Press, Toronto, 1960), p. 316.

<sup>35</sup> C. H. Cheng, C. T. Wei, and P. A. Beck, *Phys. Rev.* **120**, 426 (1960).

<sup>32</sup> A. Calverley and A. Rose-Ines, *Proc. Roy. Soc. (London)* **255**, 267 (1960).

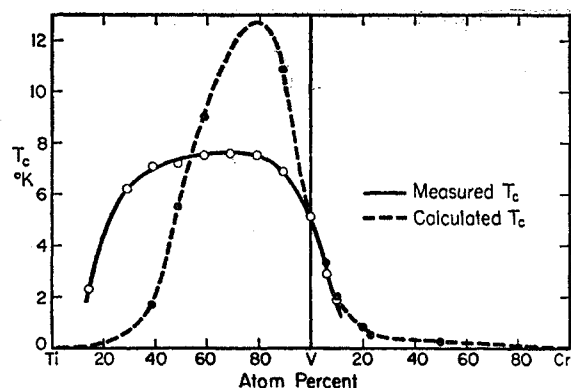


FIG. 13. Calculated and measured  $T_c$  versus composition, Ti-V-Cr.

in Table III and in Fig. 13. It should be emphasized that by the nature of our calculation, we have arbitrarily forced the theoretical curve to pass through the correct transition point for pure vanadium. The choice of some other alloy composition as a normalization point would have affected the height of the theoretical curve but not its general shape, which is determined primarily by the variation of  $\gamma$  with composition. From Table III, it is obvious that  $\gamma$  passes through a maximum between group 4 and group 5 and falls off quite steeply between group 5 and group 6.

Bearing in mind our arbitrary normalization to vanadium, it is nevertheless interesting that the theoretical curve predicts quite well the steep decrease of transition temperature produced by the addition of chromium to vanadium, at least in the initial 10% of the range. However, for higher chromium contents, the theoretical curve levels off and approaches absolute zero, predicting a small but positive value of  $T_c$  ( $\sim 10^{-8}$  K) for pure chromium. Positive  $T_c$  values are an inevitable consequence of Eq. (4) if we assume  $V$  constant and  $N(0)$  positive.

In presenting the experimental data, it was pointed out that for the five binary combinations between group 5 and group 6 metals studied by us, the transition temperature was essentially a linear function of composition. Furthermore, the results could be correlated by assigning "negative transition temperatures" to chromium, molybdenum, and tungsten. However, since measurements were made only down to 1.02°K, it is quite uncertain whether the linear dependence on composition extends below 1°K, with the disappearance of superconductivity at a definite composition, or whether

TABLE III. Summary of results.

Alloy composition (atom percent)	$\Theta$ (°K) <sup>a</sup>	$\gamma$ (millijoules mol <sup>-1</sup> deg <sup>-2</sup> ) <sup>b</sup>	$N(0)V$	$T_c$ (calc) (°K)	$T_c$ (meas) (°K)
Ti	430	3.3	0.088	0.004	0.40
Ti+38.5 V	395	7.1	0.189	1.70	7.07
Ti+48.4 V	386	9.2	0.245	5.56	7.20
Ti+58.5 V	376	10.5	0.280	9.04	7.49
Ti+89.4 V	348	11.3	0.302	10.86	6.86
V	338	9.3	0.248	$\epsilon$	5.13
V+6 Cr	342	8.4	0.224	3.36	2.90
V+10 Cr	344	7.5	0.200	1.98	1.90
V+20 Cr	351	6.4	0.171	0.91	<1.02
V+23 Cr	353	5.9	0.158	0.53	<1.02
V+50 Cr	370	4.9	0.131	0.15	<1.02
V+75 Cr	386	2.0	0.053	$10^{-6}$	<1.02
Cr	402	1.6	0.043	$10^{-8}$	<0.1

<sup>a</sup> Linear interpolation between pure metal values.

<sup>b</sup> C. H. Cheng, C. T. Wei, and P. A. Beck, Phys. Rev. 120, 426 (1960).

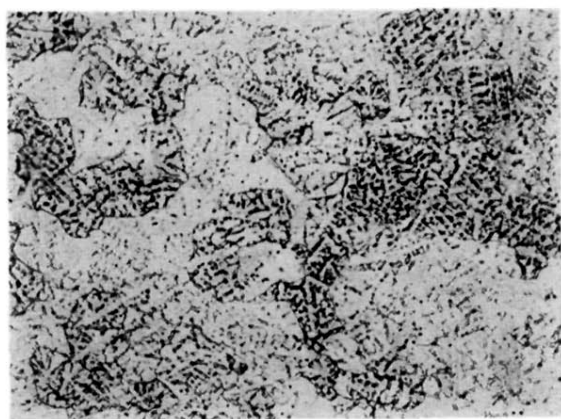
<sup>c</sup> Assumed equal to measured  $T_c$ .

the transition temperature-composition curve levels off and approaches absolute zero more gradually as suggested above for the V-Cr system. It would appear to be worth while to study one of the group 5-group 6 alloy systems below 1°K in order to check the validity of Eq. (4).

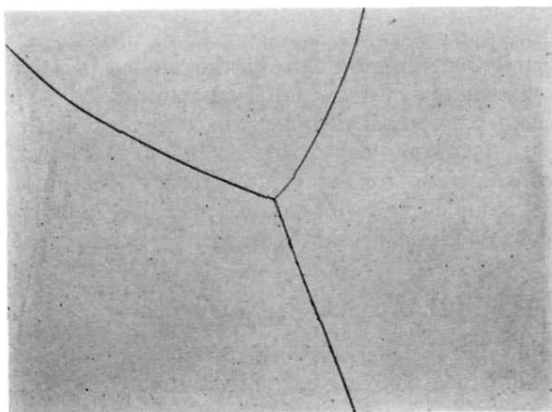
Figure 13 indicates that in the titanium-vanadium system, Eq. (4) does little more than predict the general shape of the variation of  $T_c$  with composition. It must be pointed out that the  $\gamma$  values given by Cheng, Wei, and Beck are admitted by these authors to be very approximate. However, it is doubtful if the error in  $\gamma$  is enough to account for the large discrepancy between the theoretical and experimental  $T_c$  values. The difficulty is more likely to be due either to the inadequacy of our assumption of a constant  $V$  parameter applicable to the entire alloy system or, perhaps, more basically to the unsuitability of Eq. (4) in its present form. The exponential relationship between  $T_c$  and  $\gamma$  inevitably leads to a sharp peak in  $T_c$  versus composition, whereas the experimental data suggest a rather flat maximum with a steep drop at each end of the plateau. The resolution of these questions will be a great deal easier when more accurate heat capacity data are available for the solid solution alloys described in this paper.

#### ACKNOWLEDGMENTS

We are grateful to C. B. Satterthwaite for loaning a helium-3 cryostat and to R. T. Begley and L. France for supplying samples.



(a)



(b)

FIG. 4. Metallograph for Nb+10% Cr specimen before and after annealing.