

SUPERCONDUCTING ALLOYS OF INTERSTITIAL COMPOUNDS*

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Abstract

The preparation and evaluation of some interstitial compounds is described and their potential as high transition temperature superconductors discussed. An evaluation of transition temperature measurements of pseudo-binary and ternary interstitial alloys shows that no simple direct relationship exists between transition temperature and such quantities as valence electron-atom ratio, mass and lattice volume. However, the experimental data have been successfully systematized in terms of a general empirical model which appears capable of predicting the most promising materials for attaining high transition temperatures. Preliminary data demonstrate that a large number of alloyed interstitial compounds exhibit transition temperatures in the vicinity of 18°K.

1. Introduction

THE present paper describes the first phase of a program aimed primarily at seeking new superconducting materials with transition temperatures exceeding 18°K. Obviously there would be no need for an experimental program to raise transition temperatures if they could be calculated from first principles. Such calculations are not possible at the present time, in spite of the emergence during the past decade of a very successful microscopic theory of superconductivity developed mainly by Bardeen, Cooper and Schrieffer [1], and referred to hereafter as the "BCS model". The BCS model yields an explicit expression for T_c and predicts that transition temperatures should increase when either the density of states at the Fermi surface or the electron-phonon coupling strength is increased. Unfortunately, neither the density of states nor the coupling parameter can be calculated accurately. Indeed, at present, the coupling parameter is usually estimated by using the BCS expression and calculating backwards from T_c itself.

Since the highest known value of T_c , approximately 18°K, was discovered [2] before the advent of the BCS model, it is hardly surprising that microscopic theories made no contribution to the discovery. The process was, in fact, a purely empirical one based primarily on an examination of alloys and compounds in promising zones of the periodic table. Extensive work was done in the 1930's by Meissner and his associates [3] who demonstrated that T_c values up to about 12°K could be obtained with interstitial compounds of the transition elements, primarily

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in the carbide and nitride class. In 1941, Justi and co-workers [4] discovered the transition in NbN at 15°K. In 1953, in an examination of other transition-metal compounds, Hulm and Hardy [5] discovered superconductivity in the β -tungsten structure, achieving 17°K with the compound V₃Si. This ubiquitous superconducting class was extended to include V₃Ga, Nb₃Al and Nb₃Sn by Matthias and co-workers [2,6,7], who found Nb₃Sn to exhibit a transition temperature close to 18°K. Subsequent exploratory work has failed to yield transition temperatures significantly beyond the 18° level, and it might reasonably be asked whether the time has not arrived to abandon such an approach. The authors believe that it has not. Two reasons are paramount in determining such a belief, firstly the lack of a strong theoretical prediction of an 18°K limit for transition temperatures, and secondly, the existence of a large number of untested transition metal compounds with apparent high transition temperature potential. It would take too long to review all promising superconducting materials, but it seems appropriate to indicate how a choice was made of the compounds studied in the present work.

The most obvious place to look for new high T_c materials is among those structures which have already yielded high values. There are three leading classes, firstly the transition metal alloys with the body-centered-cubic structure, secondly the β -tungsten crystal structure compounds, and thirdly, the interstitial compounds with the NaCl crystal structure. The first two classes have been investigated quite extensively [8,9], but in the case of the interstitial compounds, the situation is different. Alloyed interstitial compounds have received relatively little study in spite of their considerable potential. For example, nitrides of niobium have T_c values reported between 14.7 and 16.0°K, while Nb(C_{0.3}, N_{0.7}) remains superconducting up to 17.8°K [10]. It is significant that a considerable increase in T_c is obtained by alloying the interstitial compounds, which is in direct contrast to the behavior of the β -tungsten compounds, where alloying mainly causes a rather severe depression of T_c [9]. Alloys of interstitial compounds obviously warrant further investigation. Such compounds have the additional advantage that as a result of the extensive solid solubility in pseudo binary and ternary alloys [11-13] it is possible to study wide range solid-solution systems of interstitial compounds in which the valence electron-atom ratio, lattice volume, and mass may be varied while maintaining a constant crystal structure. Consequently, the present study has been restricted to an examination of alloyed interstitial compounds possessing the NaCl crystal structure.

2. Experimental Procedures

Details of the preparation of the component interstitial compounds used in the present work have been described elsewhere [14]. The nitrides were prepared by reacting purified nitrogen gas with the appropriate metallic hydride at temperatures varying from 1400 to 2000°C. The carbides were prepared by cold pressing the appropriate metal or oxide with spectroscopically pure carbon powder followed by several sintering treatments under vacuum at progressively higher temperatures until the reaction was completed. Subsequent preparation of the pseudo-binary and ternary alloys was accomplished by sintering cold pressed compacts of the required amounts of the component compounds at temperatures between 2000 and 2400°C in an atmosphere of purified N₂ gas. T_c measurements were made on both sintered compacts and powder samples.

X-ray examinations have been carried out on the majority of the samples in order to determine both the effectiveness of the sintering reaction in producing single phase material and the correlation, if any exists, between transition temperature and lattice volume. The lattice parameters observed for the component materials used in the present work [14] are consistently higher than those previously reported by Duwez and Odell [11]. A likely cause of the systematic deviation is the use of purer starting materials in the current study which allows a closer

approach to the stoichiometric composition. Unfortunately, chemical analyses have not yet been made to establish whether or not this is the correct explanation. As would be expected, however, the lattice parameter vs. composition curves for pseudo-binary alloys which were made from the components described above, are obtained in all cases by a slight upward displacement of the corresponding curves reported by Duwez and Odell [11]. Such an effect is typified by the X-ray data for the NbN-NbC pseudo-binary system which were obtained at the onset of the present investigation and have been subsequently published [15]. The lattice parameters of pseudo-ternary alloys based on $(\text{NbN})_{0.75}(\text{NbC})_{0.25}$ generally showed a nearly linear relationship to the concentration of the third component. Metallographic examinations which were carried out on a few alloys substantiated the X-ray data.

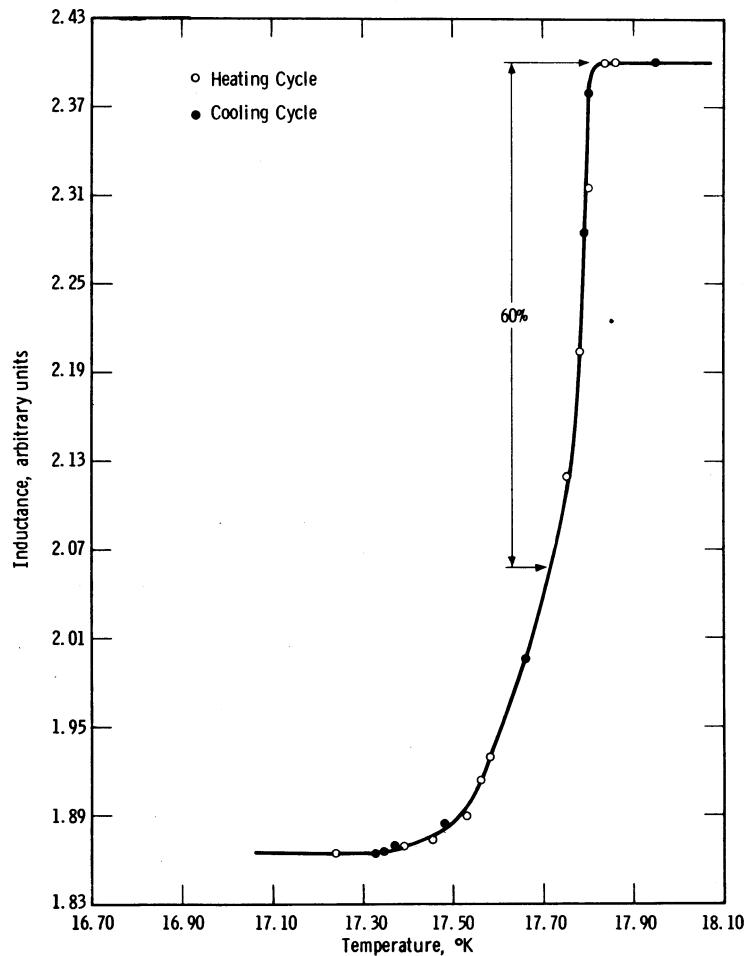


FIGURE 1

Typical hysteresis of the superconducting to normal transitions. The data were obtained using a NbN-NbC-TiC pseudo-ternary alloy. The temperature range over which the final 60% of the sample becomes normal, as indicated, is regarded as the transition temperature of the nominal composition.

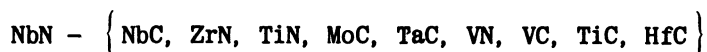
The technique used to measure superconducting transition temperatures was essentially a modified form of that originally described by Hulm and Hardy [5]. Six samples, in powder or

lump form, could be measured simultaneously by symmetrical placement around a hollow copper spool, the center of which was used as a helium gas thermometer. The flux expulsion which occurs at the onset of superconductivity was detected using a 17 c/s a.c. field in combination with a mutual inductance bridge. As indicated in Fig. 1 the hysteresis in a heating-cooling cycle was less than 0.01°K.

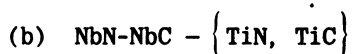
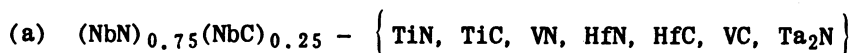
3. Experimental Results

The particular interstitial alloy systems which were chosen for investigation fall into two main categories: firstly, pseudo-binary alloys based on niobium nitride, and secondly, pseudo-ternary alloys based on carbonitrides of niobium. The specific alloy systems are listed below:

(1) Pseudo-binary alloys:



(2) Pseudo-ternary alloys:



The changes in the superconducting transition temperature of niobium nitride that are brought about by alloying additions of both transition-metal carbides and nitrides are presented in Figs. 2 and 3, respectively. All transition ranges quoted refer to the transition range of the last 60 per cent of the sample to normalize, since this is regarded as most characteristic of the nominal composition. Such an approach is clearly illustrated in Fig. 1. The low temperature tail is regarded as indicative of small composition variations.

In the NbN-NbC system, a maximum T_c value was exhibited at the composition $(\text{NbN})_{0.7}(\text{NbC})_{0.3}$ which was found to have a transition range of 17.85-17.96°K, in excellent agreement with that reported by Matthias [16,17]. Transition temperature values for other alloys in the NbN-NbC system that had not been reported until the initiation of the present study are also given in Fig. 2. A broad peak in the T_c -composition curve is clearly indicated with a composition range of approximately 13-52 mol.% NbC exhibiting $T_c > 17^\circ\text{K}$.

TiC initially produces a slightly greater dT_c/dc (where c is concentration) when alloyed with NbN than does NbC. In fact, the preliminary data suggest that the optimum T_c to be attained in the NbN-TiC system may exceed 18°K. The NbN-TiN system exhibits similar characteristics, although there is some doubt as to the true composition of the NbN-TiN alloys as evidenced by scatter in the X-ray data. The actual compositions used for both the NbN-TiN and NbN-ZrN alloys were based on the lattice parameter/composition curves of Duwez and Odell [11]. In some cases, the deviation of the nominal composition from that derived from X-ray data was several percent.

Alloys of NbN with MoC and TaC have also indicated T_c values greater than that of the base material, NbN, and in these two systems the T_c -composition relationships are quite different from other systems. For NbN-MoC alloys only a slight increase in T_c occurs for alloying contents below 10 mol.% MoC after which the T_c value drops rapidly, while the opposite effect occurs for

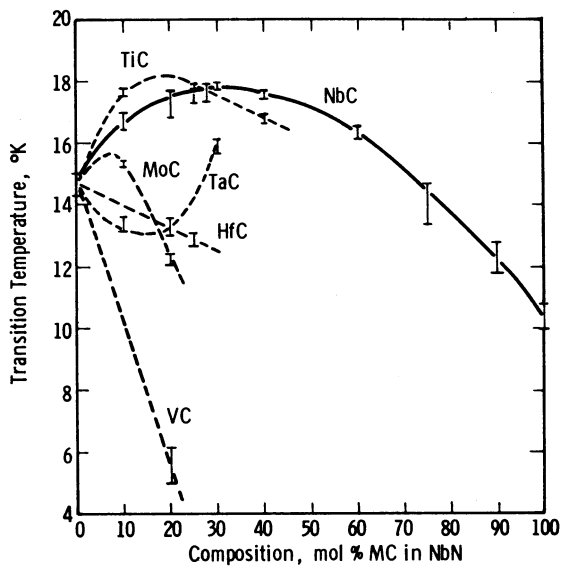


FIGURE 2

Transition temperature-composition relationships for pseudo-binary alloys of the general form $(\text{NbN})_x(\text{MC})_{1-x}$ where M is a transition metal

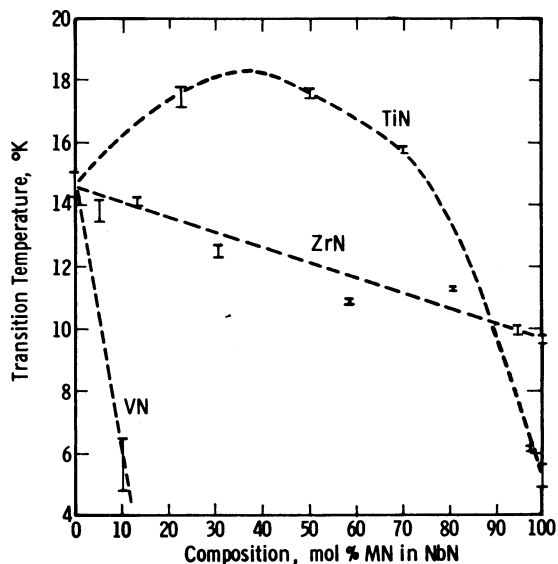


FIGURE 3

Transition temperature-composition relationships for pseudo-binary alloys of the general form $(\text{NbN})_x(\text{MN})_{1-x}$ where M is a transition metal.

NbN-TaC alloys.

Initial data for NbN-ZrN alloys are somewhat scattered but clearly show the absence of the pronounced peak effect found in the NbN-TiN system, while small additions of VN to NbN bring about a very rapid decrease in the transition temperature. HfC and VC additions to NbN bring about similar effects to ZrN and VN respectively.

The majority of the pseudo-ternary systems investigated have been based on the alloy $(\text{NbN})_{0.75}(\text{NbC})_{0.25}$. Seven different alloying additions have been made to the niobium carbide, but the alloying addition increases the transition temperature in only two instances.

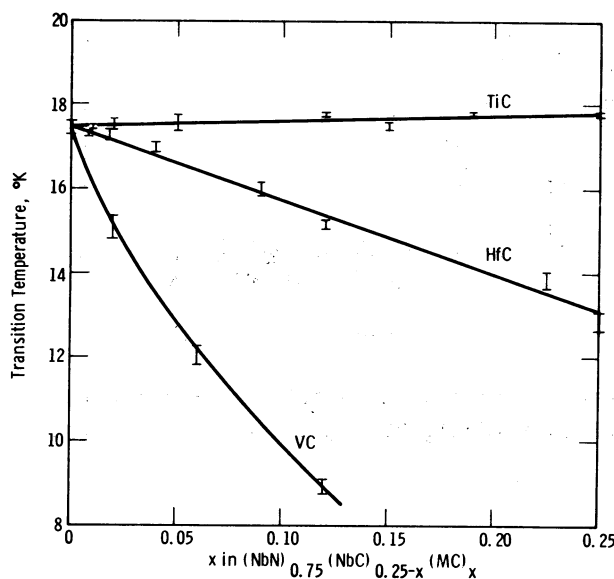


FIGURE 4

Transition temperature-composition relationships for pseudo-ternary alloys of the general form $(\text{NbN})_{0.75}(\text{NbC})_{0.25-x}(\text{MC})_x$ where M is a transition metal.

The general effects of the alloying additions are presented in Figs. 4 and 5. For $(\text{NbN})_{0.75}(\text{NbC})_{0.25-x}(\text{TiC})_x$ alloys, a very slight linear increase of T_c occurs with increasing TiC concentration, attaining a maximum value of 17.8°K at the limiting composition $(\text{NbN})_{0.75}(\text{TiC})_{0.25}$. For alloys of the type $(\text{NbN})_{0.75-x}(\text{NbC})_{0.25}(\text{TiN})_x$, a maximum T_c value of 17.8°K is also observed at the composition $(\text{NbN})_{0.60}(\text{NbC})_{0.25}(\text{TiN})_{0.15}$. In view of the apparent potential of the NbN-NbC-TiN and NbN-NbC-TiC pseudo-ternary systems, both systems were examined in detail.

The transition temperature measurements for alloys in the NbN-NbC-TiN systems are given in Figs. 6, 7 and 8 for constant concentrations of NbN, TiN and NbC, respectively. By interrelating the three sets of data it has been possible to determine the composition limits in the pseudo-ternary phase diagram that bound areas of given T_c characteristics. Such a procedure has been carried out in Fig. 9 for the NbN-NbC-TiN system using the information in Figs. 6, 7 and 8 to indicate the composition range over which alloys exist with $T_c > 17.5^\circ\text{K}$. A similar construction for NbN-NbC-TiC alloys is given in Fig. 10. It appears, therefore, that although a multitude of alloys can be made with $T_c > 17.5^\circ\text{K}$, the pseudo-ternary alloys so far examined do not

exhibit transition temperatures that exceed the maximum values found for the pseudo-binary alloy systems which form the basis of the pseudo-ternary systems. However, the two composition regions so defined in the NbN-NbC-TiC and NbN-NbC-TiN pseudo-ternary systems are different from each other. The dotted line in each figure shows the direction of constant electron-atom ratio which obviously bears only a rough relationship to the contours of constant T_c .

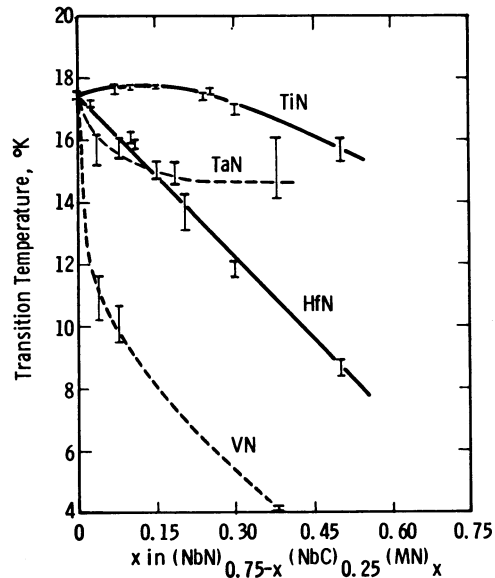


FIGURE 5

Transition temperature-composition relationships for pseudo-ternary alloys of the general form $(\text{NbN})_{0.75-x}(\text{NbC})_{0.25}(\text{MN})_x$ where M is a transition metal.

Transition temperatures of three alloys in the system NbN-ZrN-TiN have also been measured, in which the ZrN in $(\text{NbN})_{0.7}(\text{ZrN})_{0.3}$ was gradually replaced with TiN. As shown in Fig. 11, an essentially linear increase in T_c is observed with increasing TiN content. On extrapolation to the limiting composition $(\text{NbN})_{0.7}(\text{TiN})_{0.3}$, a transition temperature of 18°K is indicated, which is completely consistent with the initial observations made on the NbN-TiN pseudo-binary system (see Fig. 3).

4. Discussion

(1) Previous empirical correlations

Many attempts [8,18-28] have been made to establish useful empirical formulae containing mass, volume and electronic factors, to correlate the rapidly growing list of superconducting compounds and alloys. Undoubtedly the best known of these is the equation proposed by Matthias [24],

$$T_c \propto \frac{V^x T(N)}{M} \quad (1)$$

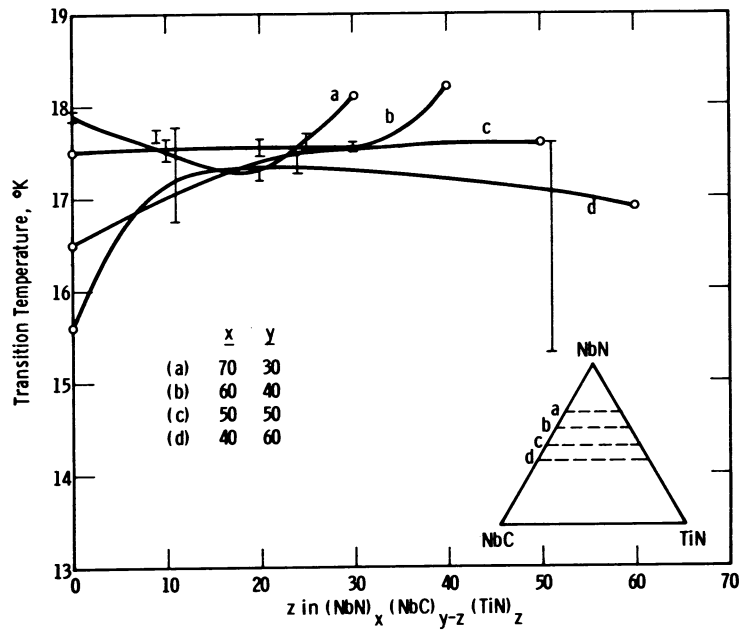


FIGURE 6

Transition temperature-composition relationships for NbN-NbC-TiN pseudo-ternary alloys at four levels of NbN concentration. The composition ranges studied are indicated on the inset phase diagram.

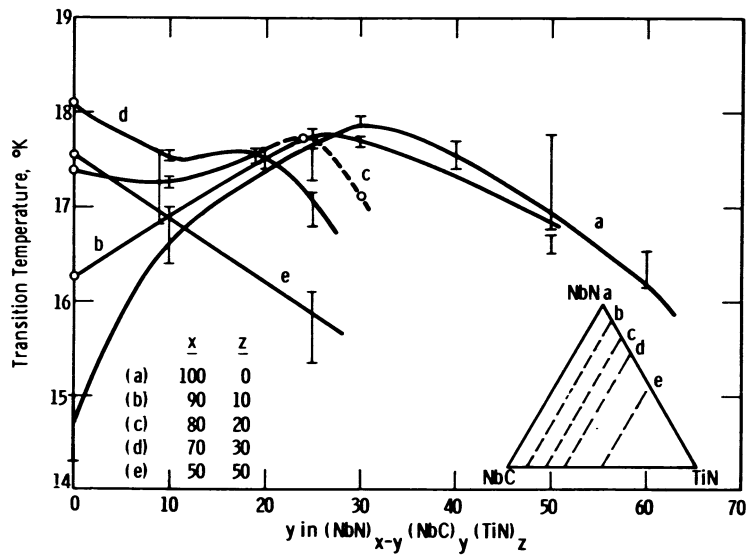


FIGURE 7

Transition temperature-composition relationships for NbN-NbC-TiN pseudo-ternary alloys at four levels of TiN concentration. The composition ranges studied are indicated on the inset phase diagram.

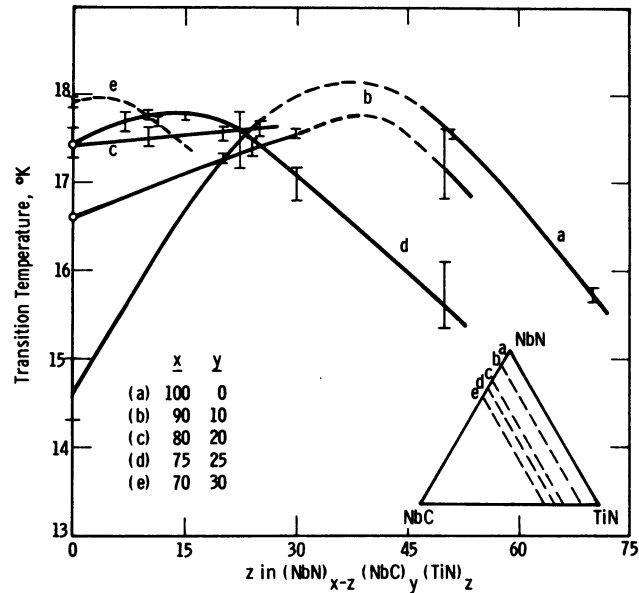


FIGURE 8

Transition temperature-composition relationships for NbN-NbC-TiN pseudo-ternary alloys at four levels of NbC concentration. The composition ranges studied are indicated on the inset phase diagram.

where M and V are atomic mass and volume respectively, and $T(N)$ is an empirical function of N , the average number of valence electrons per atom. Here, N is given by $\sum c_i N_i$ where N_i is the valency of the i -th component of atomic concentration c_i . $T(N)$ is a monotonically increasing function of N for non-transition metal superconductors, but is an oscillating function for the transition metals, a phenomenon that is presumably associated with the transition metal d -band.

While qualitatively useful, equation (1) does not give a satisfactory detailed correlation of the occurrence of superconductivity even for the elements, despite the somewhat arbitrary nature of $T(N)$. Consequently, various attempts have been made to modify equation (1) to give a more satisfactory quantitative agreement with alloy and compound data. For example, in considering solid solution transition metal alloys based upon a given solvent metal, DeSorbo [26] suggested that the factor N should be modified to allow for the change of the effective number of electrons due to expansion or contraction of the lattice by the solute atoms. Thus N is replaced by a modified factor

$$N_{eff} = V_s \sum c_i N_i / \sum c_i V_i \quad (2)$$

where V_s and V_i are the unit cell volumes of the solvent metal and the i -th component metal respectively. DeSorbo showed that for dilute alloys of niobium, where only a limited, non-

oscillating region of $T(N_{eff})$ is involved, equation (2) brings all T_c values onto a single linear function, irrespective of solute atoms.

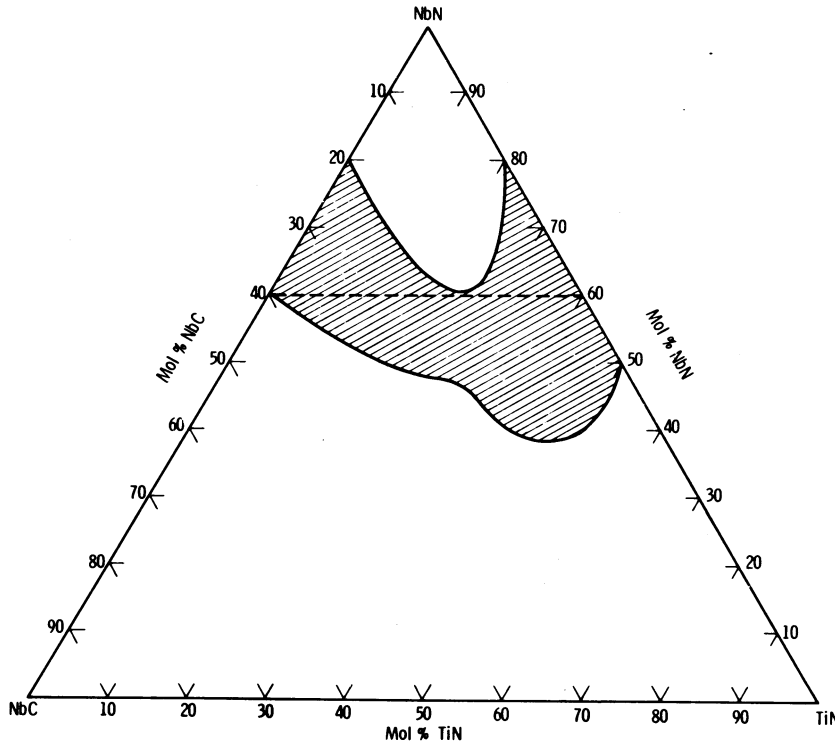


FIGURE 9

The data in Figs. 6, 7 and 8 combined to delineate the composition range in the NbN-NbC-TiN pseudo-ternary phase diagram in which the alloys have $T_c \geq 17.5^\circ\text{K}$.

Roberts [27] suggested the use of valence electron density instead of valence electrons per atom as the electronic factor for equation (1). The electron density may be written in the form,

$$d_e = p \frac{\sum c_i N_i}{\sum c_i V_i} \quad (3)$$

where p is the number of atoms per unit cell. Unlike equation (2), the last equation has the advantage that it does not have the ambiguity associated with the choice of a particular solvent. He showed that those β -tungsten compounds of the T_3X type with high transition temperatures tend to cluster around a particular value of d_e , providing that a specific transition metal occupies the T site. However, as niobium, vanadium and molybdenum are substituted in the T site, the position of the transition temperature peak occurs successively at 0.26, 0.36 and 0.43 valence electrons per cubic \AA .

Jensen and co-workers [28] have recently shown that the transition temperature, magnetic susceptibility and electronic heat capacity of several Group VIII transition metal alloys can each be reduced to a single curve by plotting as a function of valence electron density.

In attempting to apply the various empirical expressions to the present results, the initial

approach was to employ the unmodified Matthias equation. It was immediately evident, however, that the interstitial alloys examined in the present work exhibit many inconsistencies with equation (1). For example, ZrN and NbC have the same electron-atom ratio, essentially the same mass and upon alloying both increase the lattice volume of NbN. However, NbC raises the transition temperature of niobium nitride while ZrN lowers it. Similar effects are observed with VC and TiN additions to niobium nitride. Further difficulties in using equation (1) arise when the pseudo-binary systems NbN-VC, NbN-TaC, NbN-TiC, and NbN-HfC are examined. Obviously equation (1) must not be taken too seriously.

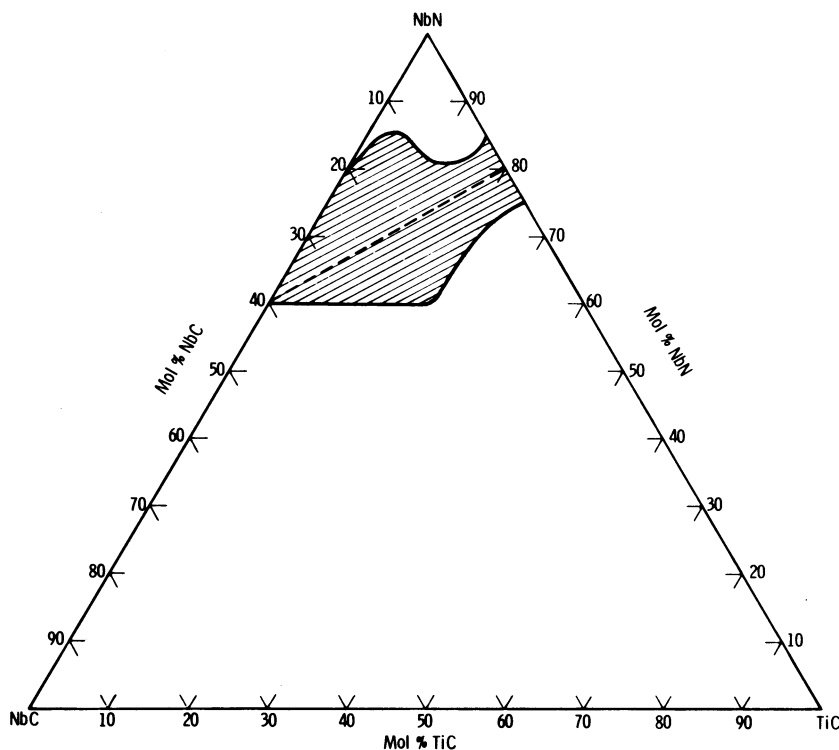


FIGURE 10

The NbN-NbC-TiC pseudo-ternary phase diagram showing the composition range in which the alloys have $T_c \geq 17.5^\circ\text{K}$.

A similar conclusion is reached if the present data are examined with respect to the modified equations (2) and (3). A plot of the transition temperatures versus either N_{eff} or electron density d_e results in considerable scatter, although a broad peak is obtained in each case, as illustrated in Fig. 12. The peak in T_c as a function of N_{eff} occurs at approximately 4.8 which is significantly different from the value of 4.4 exhibited for transition metal alloys. Likewise, the optimum value with regard to d_e occurs at a value close to 0.46 valence electrons/ \AA^3 , shown in Fig. 12, which is again at variance with optima noted by Roberts [27] in β -tungsten structure compounds.

(2) A new correlation

The major role that lattice volume appears to play in all attempts to systematize super-

conducting transition temperatures suggests that the superconducting interaction between electrons is critically dependent upon the metal interatomic distances. In the case of interstitial compounds, therefore, we tried to emphasize the change in interatomic distance of the metal atoms brought about by the introduction of interstitial atoms. As a result of adopting this approach, it was found possible to obtain an improved systematization of the superconducting transition temperatures of interstitial compounds. Since this lays emphasis upon an optimization of the spacing between the transition metal atoms, it will be referred to hereafter as the OD (optimized distance) correlation.

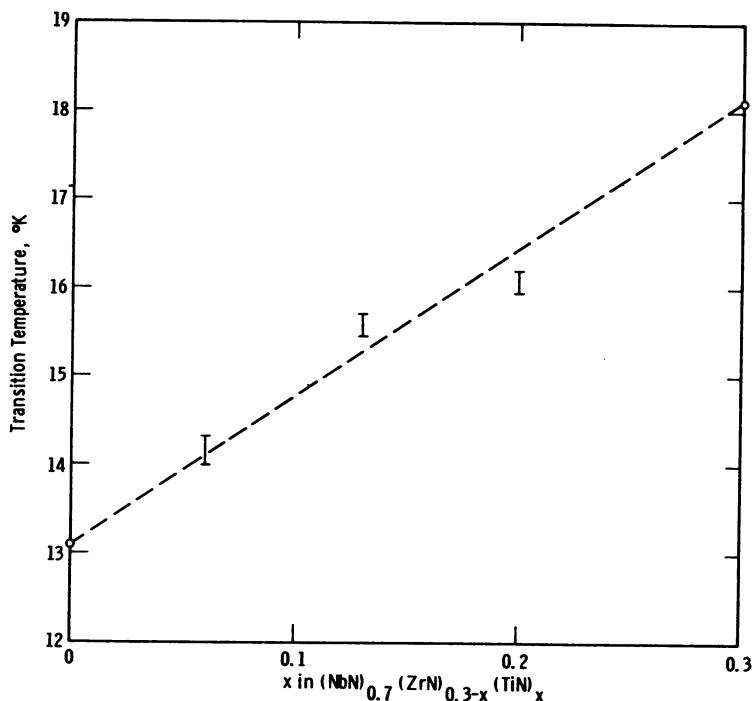


FIGURE 11

Transition temperature-composition relationships for NbN-ZrN-TiN pseudo-ternary alloys.

The basic parameter of the OD correlation is a ratio R which reflects the degree of expansion of the transition metal lattice due to the presence of various interstitial atoms. For a NaCl structure alloy the parameter is given by the relationship,

$$R = \frac{\sqrt{2} \sum c_i d_i}{a} \quad (4)$$

where d is the Goldschmidt diameter of each component transition metal atom, corrected to a coordination number of 12, and a is the actual lattice parameter of the alloy. A comparison of all the available T_c data for interstitial compounds with the parameter R immediately revealed that for a given valence number, T_c passes through a peak at a well-defined R value. Clearly if T_c attains a maximum at a definite R value it will also attain a maximum as a function of R^3 , the

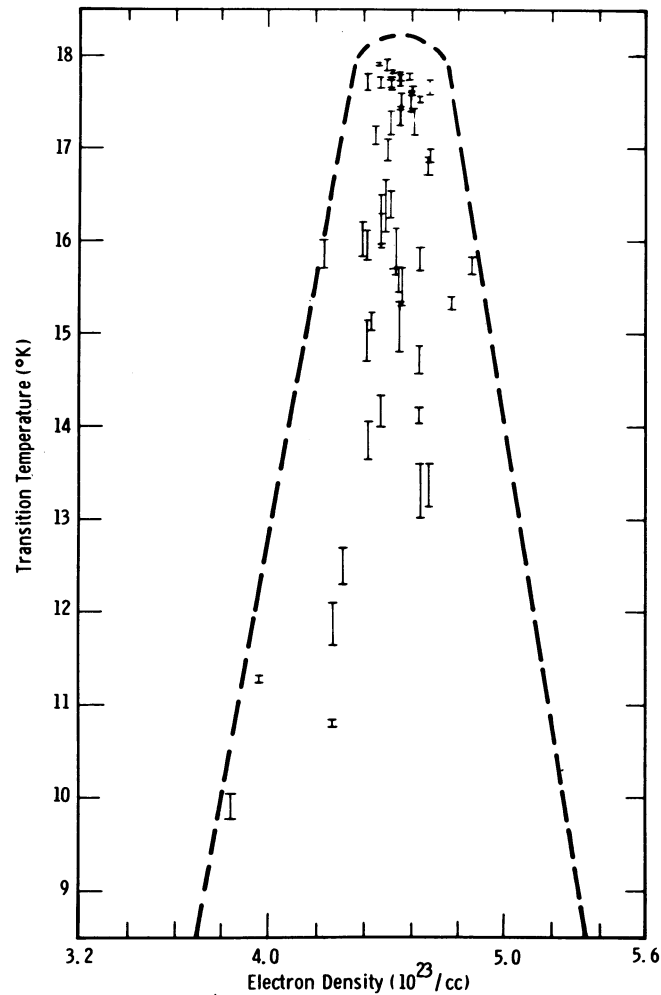


FIGURE 12

Transition temperatures of alloyed interstitial compounds as a function of electron density, d_e . The data points represent 90 different alloy compositions.

volumetric expansion of the lattice due to the interstitial atoms. In cases where the d values are very close to each other, as for example in all the interstitial compounds examined here, it is a good approximation to express R^3 in the form

$$R^3 = \frac{2\sqrt{2}}{a^3} \sum c_i d_i^3 \quad (5)$$

The evidence for a maximum of T_c as a function of R^3 in the case of simple interstitial compounds is illustrated in Fig. 13. It will be seen that the 4th and 5th Group transition metal

compounds do seem to fall upon two distinct and separate peaking curves, while compounds with R^3 shifted well away from the appropriate maximum region are not superconducting down to 1°K or lower. A rough maximum has also been sketched in for the 6th Group transition metal compounds, but for these the cubic structure data are very limited and the curve is only intended to indicate the approximate location of the peak.

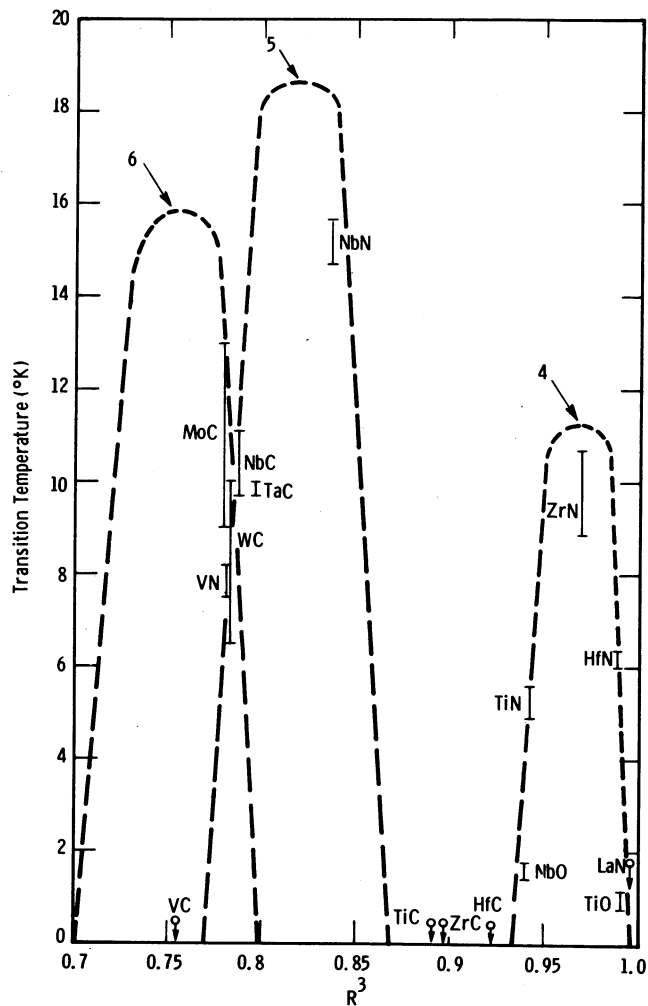


FIGURE 13

Transition temperatures of unalloyed interstitial compounds in terms of the OD correlation. The numbers associated with each curve represent the $N(M)$ values.

The three maxima of Fig. 13 are labelled with the valency of the transition metal only. At present the only justification for such an arbitrary procedure is that it works.

The apparent success of the OD correlation for the simple compounds suggested its application to the pseudo-binary and pseudo-ternary interstitial compound data. The results are shown in Fig. 14, where again only the transition metal valencies have been employed in calculating the average effective valency for each alloy system. It will be seen that there are reasonably

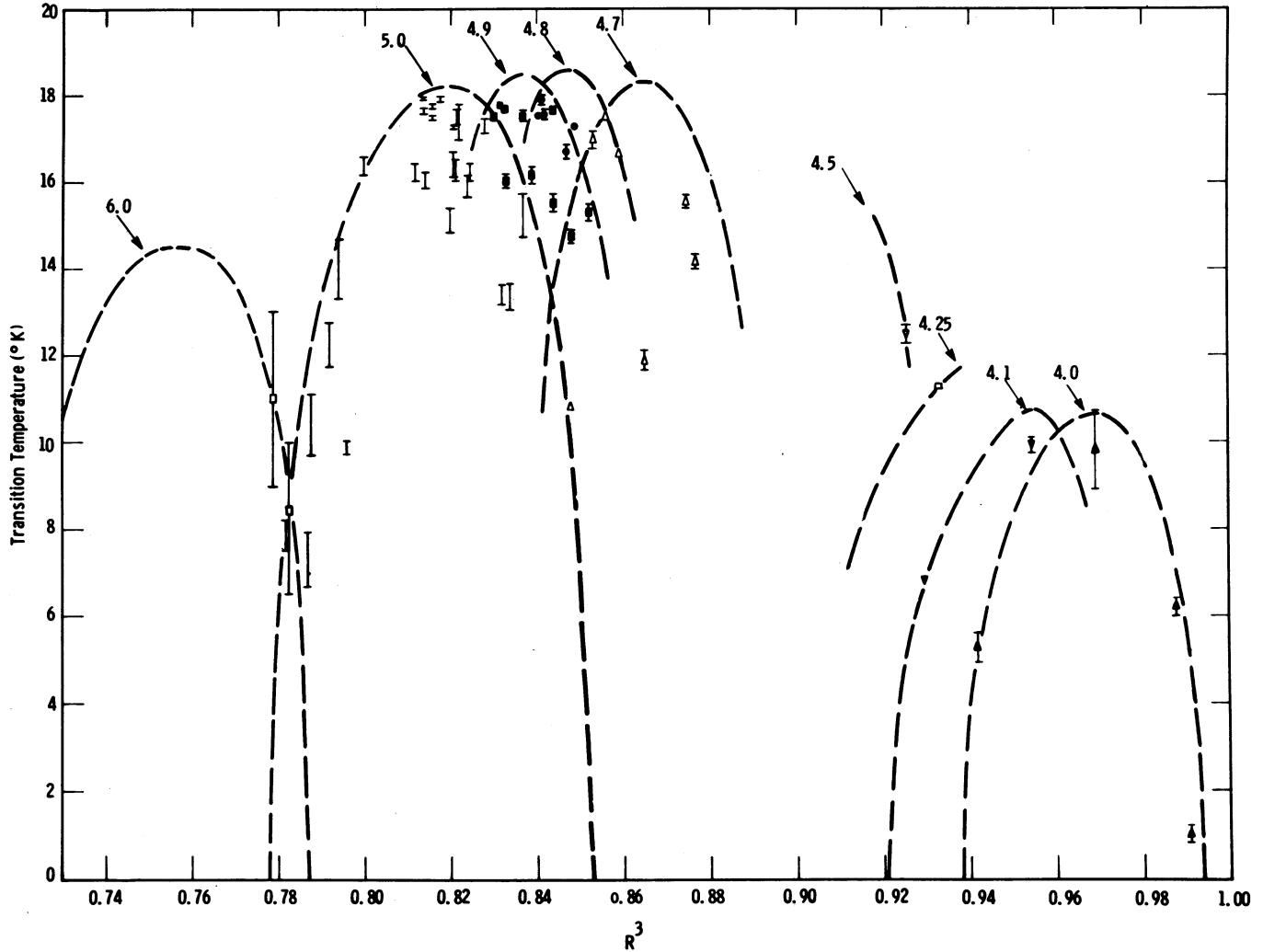


FIGURE 14

Transition temperatures of alloyed interstitial compounds in terms of the OD correlation. The numbers associated with each curve represent the $N(M)$ values.

well defined maxima for valencies between 4.7 and 5. At lower valencies the trend is similar, but not well established. Other data for intermediate valencies, which also fit similar curves, have been omitted for clarity.

Figure 14 indicates that the values of R^3 at the T_c maxima decrease with increasing transition metal effective valency. Since a peak in T_c is found for alloys with average valencies $N(M)$ of the transition metal between 4 and 5, the possibility of some T_c maxima in Fig. 14

exceeding 18°K should not be dismissed without further study.

It is interesting to note that by combining the ratio R^3 with $N(M)$ it is possible to relate the OD correlation directly to N_{eff} and electron density. The OD correlation may be expressed as a functional dependence of T_c on a normalized electron density of the form

$$D_n = R^3 N(M) \quad (6)$$

where $N(M)$ is the average valence electrons per atom for the transition metals alone, i.e.

$$\sum c_i N_i(M).$$

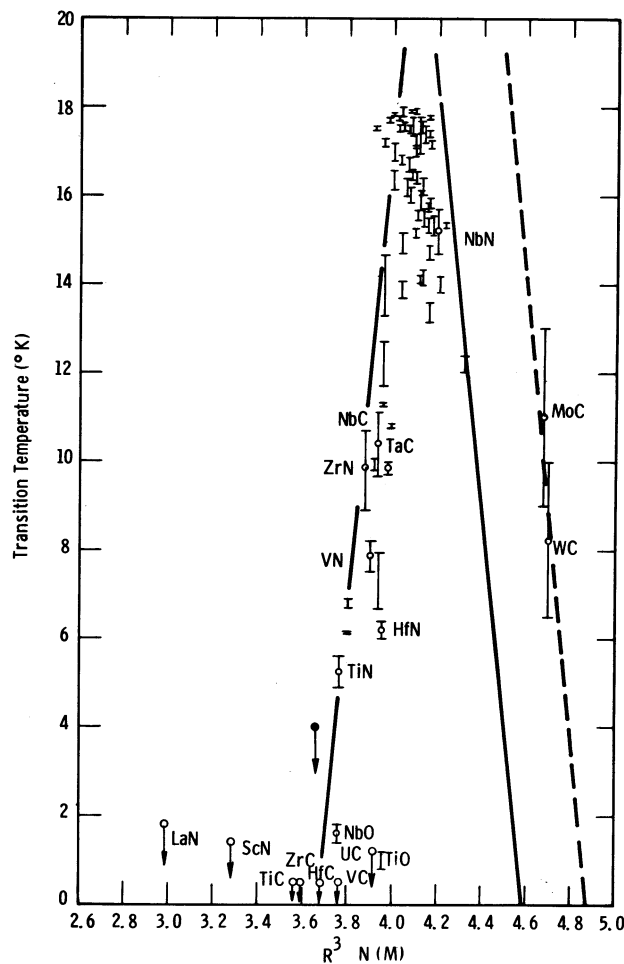


FIGURE 15

Transition temperatures of alloyed interstitial compounds as a function of $R^3N(M)$.

Figure 15 illustrates the result of applying equation (6) to the present experimental data for interstitial compounds. The higher side of the maximum in Fig. 15 is rather poorly defined

and thus two possible curves have been drawn to illustrate probable limits.

The large scatter of the data in Fig. 15 is mainly due to the variation in the heights of the maxima in Fig. 14. It is clearly not possible to combine the individual curves of Fig. 14 into a single universal function using a simple valence multiplier.

Although D_n resembles somewhat the N_{eff} and d_e functions of equations (2) and (3), there is a distinct difference which may be illustrated by writing D_n in the form

$$D_n = \sum c_i V_i \cdot \sum c_i N(M) / a^3 \quad (7)$$

where V is simply $2\sqrt{2}d^3$, the unit cell volume of a hypothetical NaCl lattice of transition metal atoms in contact with each other and a^3 is the actual unit cell volume of the interstitial compound under consideration. The basic difference between D_n and N_{eff} may now be understood. Whereas DeSorbo used a specific solvent unit cell volume, V_s , to normalize the function, in the present case the effective 'Goldschmidt volume', $\sum c_i V_i$, is used for normalization. Thus in solid solution alloys of transition metals alone, k is unity if Vegard's Law is obeyed and equation (7) reduces to the valence number of Matthias. Since equation (2) is apparently more successful in producing a general transition temperature function for such alloys than is the earlier Matthias type of plot, it seems that the OD correlation is not useful for simple metallic alloys.

Acknowledgments

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