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CRYSTAL STRUCTURES AND CRITICAL TEMPERATURES OF SOME NEW SUPERCONDUCTING COMPOUNDS

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by

Zelma Jean Johnston

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Table of Contents

		Page
	Abstract	ii
I.	Introduction	1
II.	Basic Characteristics	2
III.	Measurements of Critical Temperature	4
IV.	Occurrence of Superconductivity	5
V.	The Nb-V-Aℓ System and A15 (or β-Tungsten) Structure	7
	$Nb_3A\ell$-$V_3A\ell$ Pseudo-Binary	8
	$Nb_2A\ell$, the Sigma-Phase	9
VI.	$Mo_3A\ell_2C$ and the β-Manganese Structure	9
VII.	MoC and the B1 Structure	11
VIII.	Mo_2BC and Averaging Structures	13
IX.	Combined B1 Carbides and Intermetallics	14
X.	Summary	15
	References	18
	Appendix: Materials Used	21

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Abstract

An investigation of transition metal alloys having crystal structures favorable for superconductivity has resulted in the discovery of two new superconductors: $Mo_3A\ell_2C$, β-Mn structure, at 10.0°K and Mo_2BC, orthorhombic structure, at 5.4°K. Also, the previously reported transition temperature of $Nb_2A\ell$, σ-phase, and the extrapolated transition temperature of MoC, cubic B1 structure, were found to be too low; our observed values were 13.5°K and 14.2°K respectively.

The role of crystal structure, generally assumed to be a secondary one in determining the superconductive properties of a material, seems open to question. The transformation of MoC from hexagonal to cubic was found to be accompanied by a 7°K change in transition temperature. Such large changes cannot be accounted for by the normal electron-to-atom ratio, but must be controlled by the lesser-known parameters such as band structure and the electron density of states at the Fermi surface. Since these parameters are definitely related to the crystal structure, the importance of the atomic arrangement must not be ignored.

I. INTRODUCTION

The behavior of electrical resistivity of metals at low temperatures was among the first problems investigated by Kamerlingh Onnes after he had achieved the liquification of helium in 1908. The resistivity of the first metals tested, gold and platinum, approached a constant value at low temperature, indicating that the low temperature resistivity was controlled by impurity scattering. It was for this reason that Onnes, in 1911,[3] measured the resistivity of mercury, the only metal then available in high purity form. He found that at about 4°K the resistance abruptly drops to zero. Onnes called this state of infinite conductivity "superconductivity" and the temperature at which the phenomenon appeared he named the critical temperature. Curiously enough, Onnes soon showed that the addition of considerable impurities to mercury did not inhibit the drop to zero resistance, i.e., that the zero resistance was not just a matter of using a very pure metal. No doubt was left about the existence of a new state of mercury in which its resistance was negligible.

Although the fascinating phenomenon of superconductivity has been known for more than fifty years, an extensive search for new superconductivity compounds and materials was not undertaken until the 1950's. This study has led to the discovery of about a thousand new superconductors. Also, during the last ten years a microscopic theory of superconduction has been developed, and the potential of superconductors to produce high magnetic-field strengths has been realized.

II. BASIC CHARACTERISTICS

The first observed and most distinctive property of a superconductor is the total disappearance of resistance below a characteristic transition temperature, T_c, which is different for each material. A sharp discontinuity, Fig. 1(a), would be obtained for a single crystal of a very pure element or of a well-annealed alloy. The broad transition shown by the dashed line suggests the shape of the transition for normal materials in which there is inhomogeneity or strain. The total loss of resistance below the critical temperature has been demonstrated by inducing current to flow in a superconducting ring where it persists indefinitely without diminishing. In the most recent experiment of this type by Collins,[4] the current was observed to flow for two and a half years without any detectable decay. This places an upper limit of 10^{-21} ohm-cm on the resistivity of the superconductor. The limit was further lowered to 10^{-23} ohm-cm by Quinn and Ittner,[5] who checked the decay of a current circulating in a thin film tube. (For comparison, the low temperature resistivity of pure copper is 10^{-9} ohm-cm.)

Below T_c, the superconducting behavior can be quenched and normal conductivity restored by the application of an external magnetic field. This critical field, H_c, shows a closely parabolic dependence upon temperature, Fig. 1(b), varying approximately as

$$H_c = H_o \left[1 - \left(\frac{T}{T_c}\right)^2\right] \qquad (1)$$

where H_o is the critical field at absolute zero.

Meissner and Ochsenfeld,[6] measuring field distribution around spherical superconducting specimens, found that below T_c the magnetic flux is expelled from the interior of the superconductor and the magnetic induction B vanishes. This phenomena is called the <u>Meissner effect</u>, and in showing the superconducting

transition to be reversible, its discovery finally enabled Gorter and Casimer[7] to develop a thermodynamic treatment of superconductivity as a phase transition.

The Gibbs free energy density between the two states in zero magnetic field is

$$G_n(0) = G_s(0) + \frac{H_c^2}{8\pi} \tag{2}$$

where H_c relates to the temperature and pressure in question. As $S = -(\partial G/\partial T)_{p,H}$, differentiation yields

$$S_n(0) - S_s(0) = -(VH_c/4\pi)(dH_c/dT) \tag{3}$$

where V is the volume of the system. At $T = T_c$, $H_c = 0$, and $S_n = S_s$. At any lower temperature, $H_c > 0$, and Fig. 1(b) shows that for $0 < T < T_c$, $dH_c/dT < 0$. Hence, the entropies of the two phases are equal at the critical temperature in zero field; at any lower finite temperature the entropy of the superconducting phase is lower than that of the normal one, indicating that the former is the state of higher order. This ordering observed in the superconducting state has been shown to follow from a condensation of electrons in momentum space. Thus, the phenomenological thermodynamic treatment has given a link between the magnetic and thermal properties of a superconductor.

The critical temperature of a nontransition elemental superconductor was found to vary with its isotopic mass as $T_c \sim M^{-\frac{1}{2}}$. The transition metal elements and some alloys appear to have exponents less than $-\frac{1}{2}$. This observation of the isotope effect led in part to the Bardeen-Cooper-Schrieffer theory[8] for superconductivity which postulates certain interactions between paired electrons and lattice vibrations. The BCS theory and subsequent advances have successfully explained most of the properties of superconductive materials. The theory predicts a temperature-dependent energy gap below T_c (see Fig. 1(c)). The energy gap is denoted by $2\Delta(0)$ at 0°K, and may be experimentally determined,

for instance, by observing the attenuation of longitudinal sound waves below T_c and from superconductive tunneling experiments.

The behavior thus far described is typical of Type I, i.e., "soft" or ideal, superconductors. Another type of behavior, known as Type II or "mixed state" superconductivity, allows the superconductive state to exist in high magnetic fields. In Fig. 2 the magnetization of a superconductor as a function of field is shown for a Type II superconductor according to theoretical models of Abrikosov[9] and Goodman.[10] At the field H_{c1}, which is lower than H_c, the magnetization curve falls below the perfect diamagnetism of Type I superconductivity. The material then enters what is termed the "mixed state," a state pictured as interwoven superconductive and normal regions. At a field H_{c2}, greater than H_c, the sample reverts to the normal state. While H_c is usually less than a few thousand oersteds, H_{c2} can have values up to several hundred thousand oersteds, thus making practical high field superconductivity.

The critical temperature has become very important in utilizing high field superconductive properties because both H_c and H_{c2} increase with T_c. Thus, materials with large T_c are sought when conductors of supercurrents are needed to produce large magnetic fields. This need has led to extensive search for high T_c superconductive compounds because almost all materials with T_c above 10°K exist as compounds or modifications of compounds.

III. MEASUREMENTS OF CRITICAL TEMPERATURE

One can simply determine the onset of perfect conductivity in either of two ways: dc measurements, or low frequency ac measurements. Perfect conductivity would manifest itself in the first case as a vanishing dc potential drop, and in the second case as either a vanishing ac potential drop or a rapid change in the ac skin depth. Magnetically the perfect conductor would maintain any flux originally present inside its boundaries.

The superconductor exhibits many of the characteristics of a perfect conductor, but with the additional property that a simply connected superconductor expels any magnetic field inside its boundaries (Meissner effect). Empirically, it has been found that low frequency or dc magnetic fields penetrate a short distance into the superconductor, i.e., about 10^{-6} cm.

Two techniques used to determine the zero field transition temperature are dc resistance measurements and ac susceptibility measurements. The resistance method needs little description. It suffers the disadvantage of low sensitivity and a need for rather large measuring currents. With such large currents, sample contacts can lead to the generation of heat, introducing temperature instabilities.

Susceptibility measurements, which do not require contacts to the sample, can be quite sensitive and do give an indication of bulk properties. Unfortunately, surface phenomena can sometimes obscure such measurements through shielding of the interior. Measuring the self-inductance of a coil containing a core of the superconducting material provides only susceptance or skin effect data. However, a sharp change in susceptance accompanying the exclusion of magnetic flux at T_c gives a reasonably accurate and reproducible measurement of T_c. This is essentially the method developed by M. F. Merriam and M. von Herzen.[12]

IV. OCCURRENCE OF SUPERCONDUCTIVITY

The most important criterion for the occurrence of superconductivity has been found to be Matthias' Rule.[13] Matthias' empirical relationships have shown that high critical temperatures and a high probability of a specific material being superconductive is related to the number of valence electrons per atom in the lattice. The qualitative variance of T_c with the average number of valence electrons per atom for the elements, shown in Fig. 3, has now

been extended to include alloys and compounds where the average number of valence electrons per atom is simply the weighted average of all electrons outside a filled shell for each element in the alloy. Hulm and Blaugher[14] have shown that the observed peaks are slightly lower than the originally suggested 5 and 7 valence electrons per atom, and are more nearly at approximately 4.6 and 6.7 valence electrons per atom. Matthias also suggested from empirical considerations that T_c would vary as the atomic volume raised to the fourth or fifth power and inversely as the atomic mass. De Sorbo,[15] studying dilute solid solutions of transition metals, has shown correlations between superconducting properties, such as T_c, and solute atom size. In this study, he found that T_c correlated better with an effective e/a ratio, involving a size-dependent correction (Fig. 4), than with the usual e/a ratio.

The influence of crystal structure on superconductivity is more pronounced in compounds than in solid solutions of transition metals, particularly if the compound contains at least one transition element. The crystal structures which are particularly favorable for superconductivity include the cubic β-W type (the A15 structure), the cubic NaCℓ type (B1) and the cubic $MgCu_2$ type (C15). With the exception of NbC and NbN, which have the B1 structure, most of the high temperature superconductors have the A15 structure. Less symmetrical systems seem to be less favorable for superconductivity. In the orthorhombic systems, approximately eleven have been reported. Only one has been found in the trigonal system, $PdTe_2$,[19] and one in the monoclinic system, α - Bi_2Pd.[20] None have been reported in the triclinic system. The correlation of T_c with crystal structure, Fig. 5, follows a similar pattern with the highest T_c being obtained in the cubic system falling to lower values as the symmetry is decreased to orthorhombic, etc.

Using these empirical considerations in a search for new superconductors, newly reported transition-metal alloys were reviewed for favorable crystal structures.

V. THE Nb-V-Aℓ SYSTEM AND A15 (or β-Tungsten) STRUCTURE

The early discovery[21] of the high T_c in Nb_3Sn has led to an extensive search for A15 type intermetallic compounds. Most of these compounds are superconductive and a substantial number have critical temperatures above 10°K.

In the Nb-V-Aℓ ternary system there are essentially two areas of interest. First, the pseudo-binary $Nb_3A\ell$-$V_3A\ell$ is of interest because of the recently reported existence of the compound $V_3A\ell$, which has an A15 structure.[22] This compound was not found in earlier investigations of the V-Aℓ binary system.[23-25] Starting with $Nb_3A\ell$ we added vanadium, noting the change in T_c with the hope of stabilizing $V_3A\ell$ with an A15 structure. Interest in $V_3A\ell$ came from noting electronic and structural similarities with systems such as Nb-V-Ga (Table I). Thus, it was expected that the T_c of $V_3A\ell$ would be higher than the 17.5°K observed for $Nb_3A\ell$. Secondly, the Nb-Aℓ binary contains a sigma phase, $Nb_2A\ell$, which has the highest reported T_c of any sigma phase. Although much work has been done with additions of a third alloying element to the A15 compounds, no reports of effects of third elements in other intermetallic compounds have been made. Thus, it was of interest to determine the effect of the addition of vanadium to the T_c of $Nb_2A\ell$.

Table I

NIOBIUM			VANADIUM		
A15 Composition	Lattice Parameter	T_c(°K)	A15 Composition	Lattice Parameter	T_c(°K)
Nb_3Ga	5.171 Å	14.5[26]	V_3Ga	4.816 Å	16.8[26]
$Nb_3A\ell$	5.187 Å	17.5[27]	$V_3A\ell$	4.90 Å[22]	?

Nb$_3$Aℓ-V$_3$Aℓ Pseudo-Binary

The alloys were made in an arc furnace under an argon atmosphere to minimize impurity contamination. Each sample was melted four times and homogenized for 80 hours at 1350°C in vacuum.

On the Nb-rich side we obtained the A15 structure, which showed a transition temperature of 17.5°K at the composition $Nb_{0.73}Aℓ_{0.27}$ (a = 5.185 Å), in good agreement with results as shown in the literature.[27-29] As vanadium was added, the lattice parameter decreases to a = 5.136 Å, showing that the A15 structure dissolves approximately 30% vanadium in solid solution. The transition temperature remained essentially constant with additions up to 10% vanadium, then it decreased rapidly as shown in Fig. 6.

For the A15 structure, extensive empirical correlations have been carried out by Roberts,[18] showing that T_c varies periodically with both e/a and e/(Å)^3, Fig. 7 and 8.. Since the e/a ratio remains constant even with additions of vanadium, it would be instructive to look at the T_c vs average number electrons per unit volume. This plot shows a threefold peaking of T_c with most of the high-temperature materials centering around 0.26 valence electrons/(Å)^3. Nb$_3$Aℓ has an e/(Å)^3 ratio equal to 0.250. With addition of vanadium this is seen to increase to 0.277, thus, the e/(Å)^3 ratio is becoming less favorable and a rapid decrease in T_c is observed.

On the V-rich side, x-ray analysis showed a bcc solid solution at the composition $V_{0.73}Aℓ_{0.27}$. The lattice parameter obtained (a = 3.055 Å) is in good agreement with results of earlier investigations.[23,25] Further heat treatment at 800°C produced no observable change in structure. The bcc structure was found to exist to the composition $(Nb_{0.5}V_{0.5})_3Aℓ$. The variation of the lattice parameter for this solid solution is shown in Fig. 9. These samples showed no superconducting transition above 4.2°K.

Our investigation shows that the A15 structure $V_3A\ell$ cannot be formed by arc melting with the limited heat treatment tried. Similar results were obtained by Geballe.[30] According to Nowotny,[31] the phase $V_3A\ell$ is probably stabilized by small amounts of impurities (C, N, O), but in our experiments these interstitials did not go into solution and would not therefore act as a catalysis for the stabilization of the A15 structure.

$Nb_2A\ell$, the Sigma Phase

The sigma phase in the binary Nb-$A\ell$ system showed a lattice parameter change from a = 9.318 Å, c = 4.813 Å to a = 9.295 Å, c = 4.819 Å while the transition temperature decreased from 13.5°K to less than 4.2°K with the addition of aluminum. The maximum critical temperature obtained is higher than the 12°K reported by Corenzwit,[27] but is considerably lower than that reported by Raetz and Saur.[28] Addition of vanadium to these compounds rapidly decreased the transition temperature to less than 4.2°K.

The rapid decrease in transition temperature observed for both addition of $A\ell$ and V would indicate that T_c in the σ-phase is more sensitive to composition variation than in the A15 compounds. Superconducting compounds with the σ-phase do not show the precise empirical correlations that are found in the A15 compounds and the σ-phase $Nb_2A\ell$ does not fit into the limited correlations that have been made by Roberts[18] on this phase.

VI. $Mo_3A\ell_2C$ AND THE β-MANGANESE STRUCTURE

The A12, or α-Mn, structure is considered a favorable structure for the occurrence of superconductivity in transition metal compounds, but no investigations of its high temperature modification A13, or β-Mn, have been made.*

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* High temperature modifications have been investigated and found favorable in the Pd-As system by Raub and Webb.[32]

An investigation of ternary compounds of the form $M_3A\ell_2C$ (M = Mo, Nb, Ta, V, Ti or Cr) recently found by Jeitschko et al.,[33,34] has led to the discovery of a new superconductor, $Mo_3A\ell_2C$, which crystallizes in β-Mn (A13) structure.[33]

The samples, with the exception of $V_3A\ell_2C$, were prepared by hot-pressing the metal powders in graphite molds; $V_3A\ell_2C$ was made by arc-melting powder compacts in an argon atmosphere. In addition, sintered samples of $Nb_3A\ell_2C$ and $Ta_3A\ell_2C$ were prepared from powder compacts. All samples were annealed at 1000°C in vacuum and furnace-cooled.

A superconducting transition was observed at 10.0°K for the compound $Mo_3A\ell_2C$. The lattice parameter for the β-Mn cubic cell was a = 6.867 Å, which is in good agreement with the value reported by Jeitschko et al.[34] These investigators also found the β-Mn structure at the compositions $Nb_3A\ell_2C$ and $Ta_3A\ell_2C$, but reported that the phase crystallized with a second phase, the "H-phase," which has a hexagonal subcell. In the present investigation, the H-phase could be identified in both hot-pressed and sintered samples. This phase has now been identified[35] as having the composition $M_2A\ell C$ (M = Nb, Ta, V, Ti or Cr). The β-Mn structure could not be detected in any of the samples of $Nb_3A\ell_2C$ or $Ta_3A\ell_2C$ and none were superconducting above 4.2°K. Only the H-phases were observed for the compounds $V_3A\ell_2C$, $Ti_3A\ell_2C$ and $Cr_3A\ell_2C$ and no transitions were found above 4.2°K.

To our knowledge, this is the second compound of the β-Mn type found to show a superconducting transition, the first being $A\ell_{0.5}Ge_{0.5}Nb_3$,[36] which has a transition temperature of 12.6°K. The occurrence of superconductivity in both compounds at 10°K or higher indicates that the β-Mn structure is favorable for the occurrence of superconductivity at relatively high temperatures.

VII. MoC AND THE B1 STRUCTURE

MoC, unlike most of the transition metal monocarbides, has a hexagonal crystal structure with a transition temperature of 9.26°K.[37] In pseudo-binary systems of MoC with the monocarbides of the IVa and Va transition metals, the cubic B1 structure exists to nearly 90 mole percent MoC. Matthias et al.[38] formed solid solutions of MoC with NbC, TiC, ZrC, and VC and retained the cubic phase to about 85 mole percent MoC. By measuring T_c versus composition they predicted that the hypothetical cubic modification of MoC would have a critical temperature of 10.6°K.

The prediction that the cubic modification of MoC would have a critical temperature higher than that of the hexagonal form is not surprising. After the A15 structure those carbides and nitrides of the transition metals that crystallize in the B1 structure have the highest superconducting critical temperatures. For example, the critical temperature for NbN is 15.6°K[39] and for NbC it is 10.3°K,[37] and in a solid solution of NbC and NbN the T_c rises to a maximum of 17.8°K.[39] The unusual fact about MoC is not the predicted critical temperature of its cubic modification but rather the high critical temperature of its hexagonal form. With the exception of technetium and MoN, elements and compounds crystallizing in a hexagonal structure seldom exhibit superconductivity above 5°K.

Recent experiments on the Mo-C system[40-42] have established that the B1 modification, α MoC_{1-x}, crystallizes from the molten state at about 2600°C. In the temperature range between 2000 and 2200°C, α MoC_{1-x} transforms very rapidly into the related hexagonal η Mo_3C_2. Below 1600°C, η Mo_3C_2 decomposes very slowly into Mo_2C and C. It was further established that the α-form could be stabilized by small amounts of boron, uranium, or thorium.[43] From these experiments on the stability of α MoC_{1-x}, it was possible to quench in the MoC cubic modification and determine its critical temperature experimentally.

A series of samples in the Mo-C binary system were hot-pressed above their reaction temperatures until they began to melt. They were then quenched from three different temperatures: 1650°C, 2200°C and 2650°C. The samples quenched from 1650 and 2200°C were quenched in liquid Sn and the samples from 2650°C in oil. After the quenching procedure the outer surface of the sample was ground off to remove any contamination from Sn or oxygen. The samples quenched in Sn were in one piece but the samples quenched in oil were in the form of small beads. The phases present in the samples were identified by x-ray techniques.

The samples quenched from 2650°C were mainly cubic but contained some of the hexagonal phase since the transformation from the cubic to the hexagonal phase involves only a shift in the sequential ordering and hence proceeds very rapidly. The critical temperature of the α MoC_{1-x} was 14.2°K. No variation was observed in T_c with either a change in composition or the addition of boron. The transitions were broad and extended from 17.5°K to 12.2°K. The broad transitions were due partly to the partial transformation to the hexagonal phase and partly to the bead-like nature of the specimen.

The samples quenched from 1650°C showed only the hexagonal η Mo_3C_2 with a critical temperature of 8.8°K. The width of the transition was approximately $\frac{1}{2}$°K showing that these samples were in equilibrium. This temperature is slightly lower than that reported by Matthias[36] for arc-melted specimens.

The critical temperatures for the samples quenched from 2200°C varied from 9.4 to 11.7°K. These samples were mainly η Mo_3C_2 but had partially transformed into α MoC_{1-x}. One of the samples with a composition of $Mo_{.60}C_{.40}$ and a transition temperature of 11.7°K showed the greatest amount of transformation to the B1 phase of any of the samples quenched from this temperature.

The observed critical temperature of 14.2°K for α MoC_{1-x} is the highest known critical temperature for a carbide and is one of the highest critical

temperatures for any binary phase. This value is exceeded by only six A15 phases and NbN. Since the transition to the hexagonal phase from the cubic phase was never completely arrested, it is possible that the critical temperature of pure α MoC_{1-x} is even higher.

The probable explanation for the unusually high T_c for η Mo_3C_2 is that its crystal structure is very closely related to α MoC_{1-x}. There are examples where superconductivity has been observed in the same element or compound with different crystal modifications, for example, La (fcc and hcp).[44] This is, however, the first observation where T_c varies with degree of transformation from one phase to another. This variation would indicate that there is a gradual electronic change which averages over the structural change.

The critical temperature of pure α MoC_{1-x} is at least 50% higher than the pure hexagonal form. It would be difficult to explain this differential in T_c on the basis of a simple electron-to-atom ratio. At least for the carbides, it would seem that the crystal structure is more important in determining T_c than the e/a ratio. It might be more useful to discuss variation in T_c with crystal structure rather than applying e/a rules to cases where the crystal structure and band structure change.

VIII. Mo_2BC and AVERAGING STRUCTURES

The ternary compound, Mo_2BC, was identified by Jeitschko et al.[45] as orthorhombic and the positions of the molybdenum atoms were established. On the basis of geometric considerations, they also established the most probable sites for the boron and carbon atoms. The boron atoms form the usual boron chains usually found in monoborides; the carbon atoms occupy octahedral sites as found in the NaCℓ structure of the monocarbides.

Recently, Arrhenius et al.[46] have postulated a finite critical temperature for gold on the basis of a study of the variation of T_c with the variation of the structure of $BaAu_5$. The concept that the superconducting

transition temperature in one phase can be used to predict the transition temperature in another phase can be tested by measuring the T_c of Mo_2BC. The α MoC_{1-x} has been found to be superconducting at 14.2°K while the monoboride MoB has been found to be normal at 1.28°K.[37] Since the crystal structure of Mo_2BC is a combination of the monocarbide and the monoboride, the T_c of Mo_2BC was measured to see if it could be explained as an average similar to the crystal structure.

Samples of molybdenum powder, amorphous boron powder and lampblack at the formula Mo_2BC were hot-pressed in graphite dies and found to be superconducting at 5.4°K. Thus, the electronic properties of Mo_2BC appear to be intermediate between that of a boride and that of a carbide.

Assuming that the electronic properties are nearly an average of MoB and MoC, the critical temperature of Mo_2BC should form a similar average. Then, using a logarithmic average, as would be suggested by B.C.S. theory,[8] one could predict a superconducting transition temperature for MoB of approximately 0.5°K.

IX. COMBINED B1 CARBIDES AND INTERMETALLICS

The ternary compounds of the form $M_3A\ell_2C$ (M = Mo, Nb, Ta, V, Ti, or Cr)[33,34] seem to lend themselves to a study of ternary systems in which the superconducting carbides could be combined with the superconducting intermetallics. With this in mind, the Nb-rich corner of the Nb-Aℓ-C ternary system was investigated.

The samples were prepared by hot-pressing metal powders in graphite crucibles or arc-melting cold-pressed compacts. All samples were annealed at 1000°C and furnace-cooled.

The phase diagram (Fig. 9) obtained at this temperature did not show the reported $Nb_3A\ell_2C$[34] having a β-Mn structure, but the H-phase, later identified as $Nb_2A\ell C$,[35] was obtained. The transition temperatures of the binary

alloys were seen to change with composition as noted in Table II. The hexagonal compound, $Nb_2A\ell C$, showed no transition above 4.2°K.

Table II

Compound	Structure		T_c (°K)
Nb-Aℓ (solid solution)	bcc	Nb-rich Aℓ-rich	9 6
NbC_x	B1	$x \sim .7$ $x \sim 1.0$	6 11
$Nb_3A\ell$	A15	Nb-rich Aℓ-rich	12.5 17.5
$Nb_3A\ell$	σ	Nb-rich Aℓ-rich	13.5 < 4.2

X. SUMMARY

Although it was postulated soon after the discovery of the high T_c of Nb_3Sn that the chain-like arrangements of the niobium atoms play an important role in the superconducting behavior, its importance has since been minimized with the discovery of high T_c compounds in body-centered cubic solid solutions as well as many examples in materials having hundreds of atoms in a complex unit cell arrangement. Thus, it has been assumed that the crystal structure plays only a secondary role in determining the superconductive properties of a metal. The interrelated controlling factors are the band structure, the valence, and the electron density of states at the Fermi surface.

The effect of valence has been empirically correlated by Matthias[11] with a remarkable degree of success and theoretically studied by Pines[47] using the B.C.S.[8] theory, but the band structure and electron density of states at the Fermi surface are little known quantities in the superconducting alloys.

Thus, since the crystal structure, a parameter well-known in alloys, has a definite bearing on both the band structure and the density of states at the Fermi surface, its importance in determining the occurrence of superconductivity cannot be overlooked.

A striking example of the effect of crystal structure can be seen in the Mo-C system where the change from hexagonal to cubic is accompanied by an approximately 7°K change in critical temperature. This change cannot be accounted for by a simple valence change and is therefore probably best accounted for by a drastic change in band structure accompanying the hexagonal-to-cubic transformation. Since the band structure is not known in either the hexagonal or cubic modification, it cannot be used for the prediction of this change in critical temperature. But an empirical correlation between T_c and crystal symmetry (Fig. 5) is useful in predicting a higher T_c in the cubic modification.

Other systems which might exhibit such a change are the high temperature hexagonal-to-β-Mn (cubic) transformation in the Nb-Aℓ-C and Ta-Aℓ-C system. In these systems the hexagonal phase is not superconducting above 4.2°K, but a high temperature quench should stabilize the β-Mn form which should be superconducting at a temperature substantially above 4.2°K. Quenching in the β-Mn structure as well as testing the hexagonal phase below 4.2°K are proposed projects for the immediate future.

During this investigation of favorable crystal structures for the occurrence of superconductivity, two new superconductors were found: $Mo_3Aℓ_2C$, β-Mn structure, at 10.0°K and Mo_2BC, orthorhombic structure at 5.4°K. Also, the reported transition temperatures of the $Nb_2Aℓ$ phase (12.5°K), and MoC, cubic B1 structure (10.6°K by extrapolation), were lower than our values, 13.5°K and 14.2°K respectively.

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APPENDIX

Materials Used:

Aluminum, Alcoa, powder, 99.8% pure

Boron, United Mineral and Chemical, powder, 99.5% pure

Carbon, Fisher Scientific Company, Lampblack

Chromium, A. D. Mackay, 325 mesh powder, 99.8% pure

Molybdenum, General Electric, 325 mesh powder, 99.8% pure

Niobium, Kawecki Chemical Company, 400 mesh powder, 99.9% pure

Tantalum, Wah Chang Corp., 325 mesh powder, 99.9% pure

Titanium, United Mineral and Chemical, 325 mesh powder, 99.5% pure

Vanadium, Oregon Metallurgical Corp., 200-400 mesh powder, 99.5% pure

Figure Captions

Fig. 1 Schematics of (a) loss of resistance at T_c; (b) variation of H_c with temperature; (c) variation of the energy gap with temperature.

Fig. 2 Magnetization curve for a soft superconductor (dashed) and magnetization curve for an Abvikosov-Goodman model superconductor (solid) after Livingston.[10]

Fig. 3 Qualitative behavior of T_c as a function of the average number of valence electrons per atom as proposed by Matthias.[11]

Fig. 4 The change in electron-atom ratio with and without solute size-dependent corrections compared to the critical temperature for some solid solutions of niobium after DeSorbo.[15]

Fig. 5 Correlation of transition temperature, T_c, with crystal structure showing a decrease of T_c with decrease in symmetry.

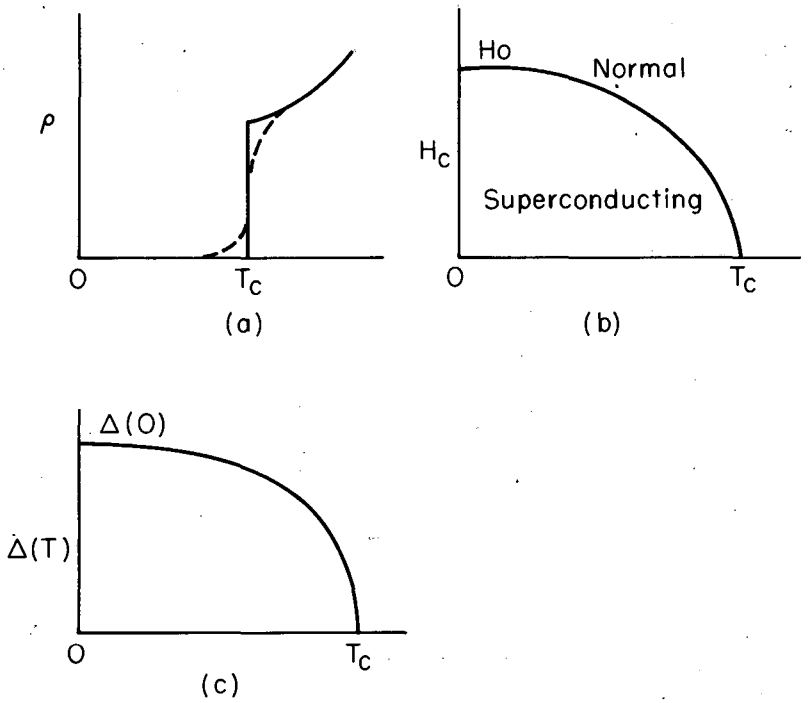
Fig. 6 Variation of transition temperature (T_c) with addition of vanadium for the A15 compound $Nb_3A\ell$.

Fig. 7 Critical temperature dependence on average number of valence electrons per atom for A15 (β-W)-type compounds.[18]

Fig. 8 Critical temperature as a function of electron density for A15 (β-W)-type compounds. (Note: Dashed lines represent apparent envelopes of experimental points only.)[18]

Fig. 9 Variation of lattice parameter with addition of niobium for the bcc solid solution $V_{0.73}A\ell_{0.27}$.

Fig.10 Equilibrium diagram for the Nb-rich corner of the Nb-Aℓ-C ternary system showing phases present and T_c data obtained.



MU-34091

Fig. 1. Schematics of (a) loss of resistance at T_c;
(b) variation of H_c with temperatures;
(c) variation of the energy gap with temperature.

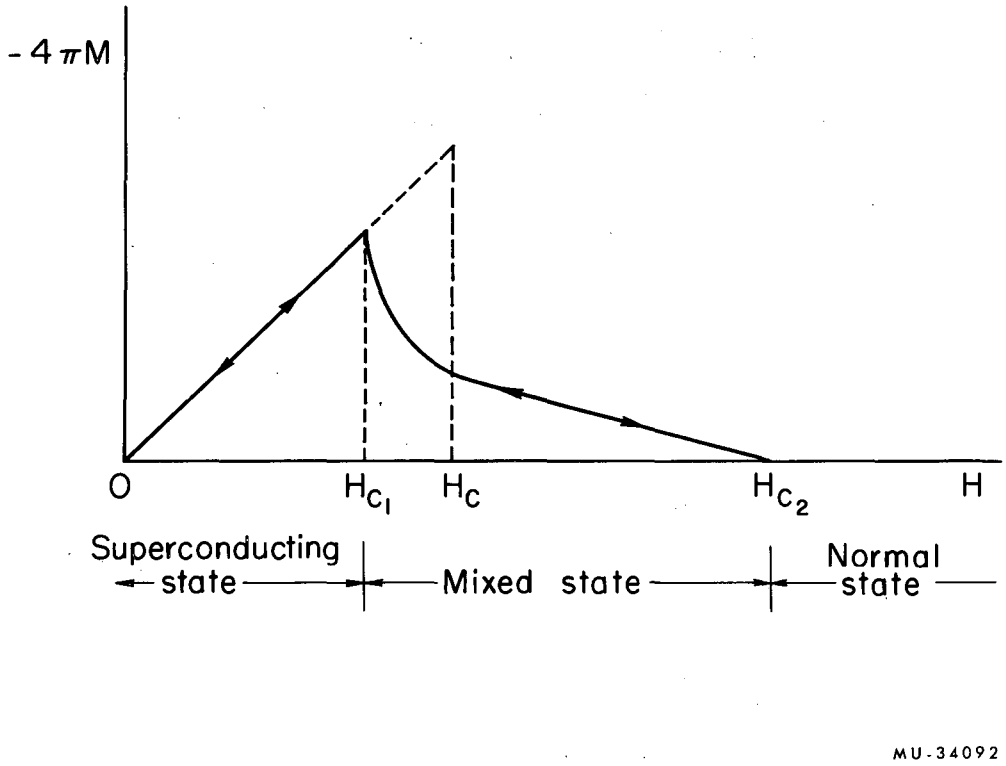
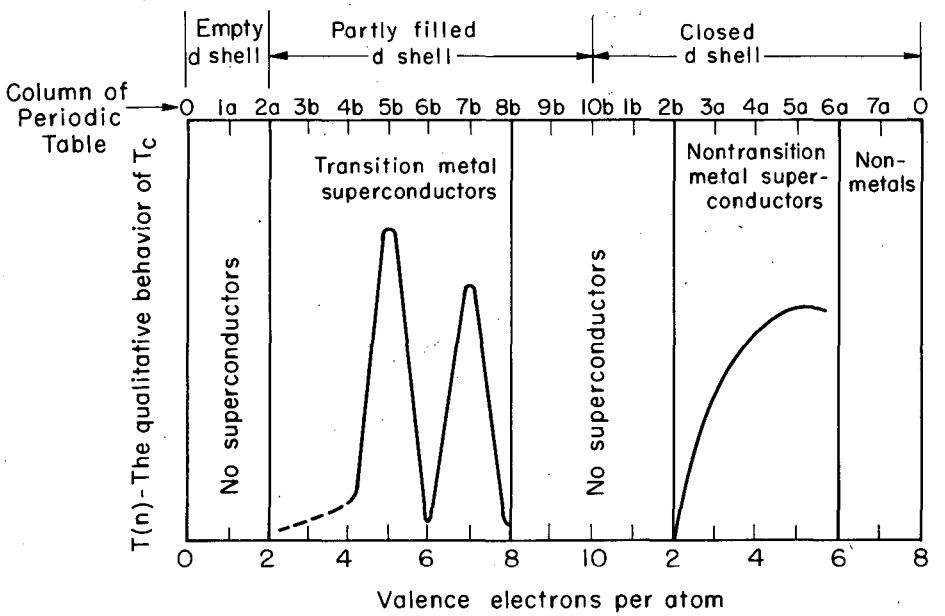
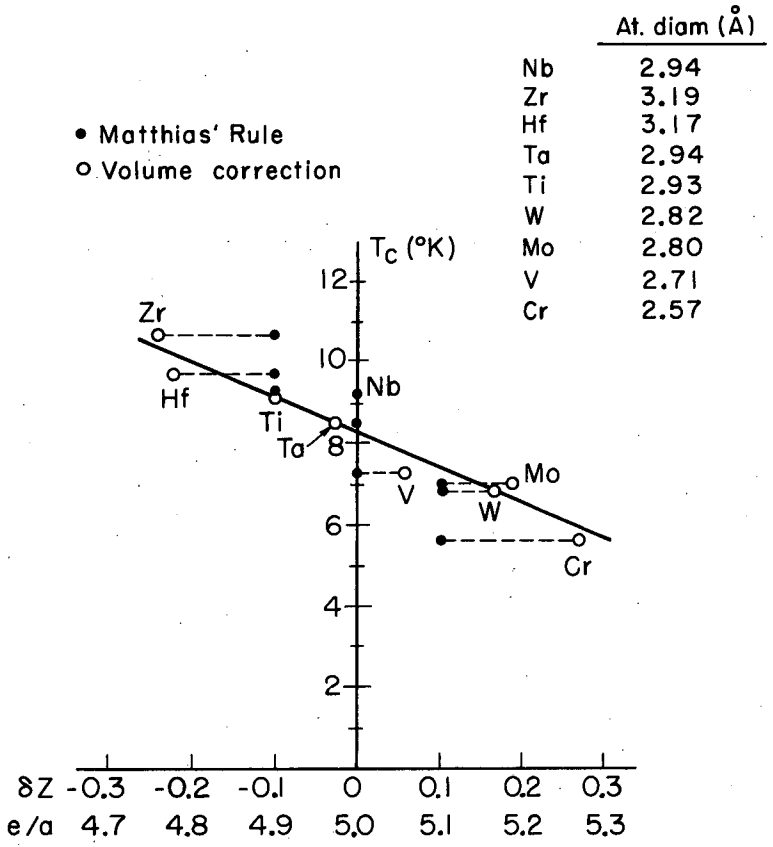


Fig. 2. Magnetization curve for a soft superconductor (dashed) and magnetization curve for an Abvikosov-Goodman model superconductor (solid) after Livingston.[10]



MU-34093

Fig. 3. Qualitative behavior of T_c as a function of the average number of valence electrons per atom as proposed by Matthias.[11]



MU-34076

Fig. 4. The change in electron-atom ratio with and without solute size-dependent corrections compared to the critical temperature for some solid solutions of niobium after DeSorbo.[15]

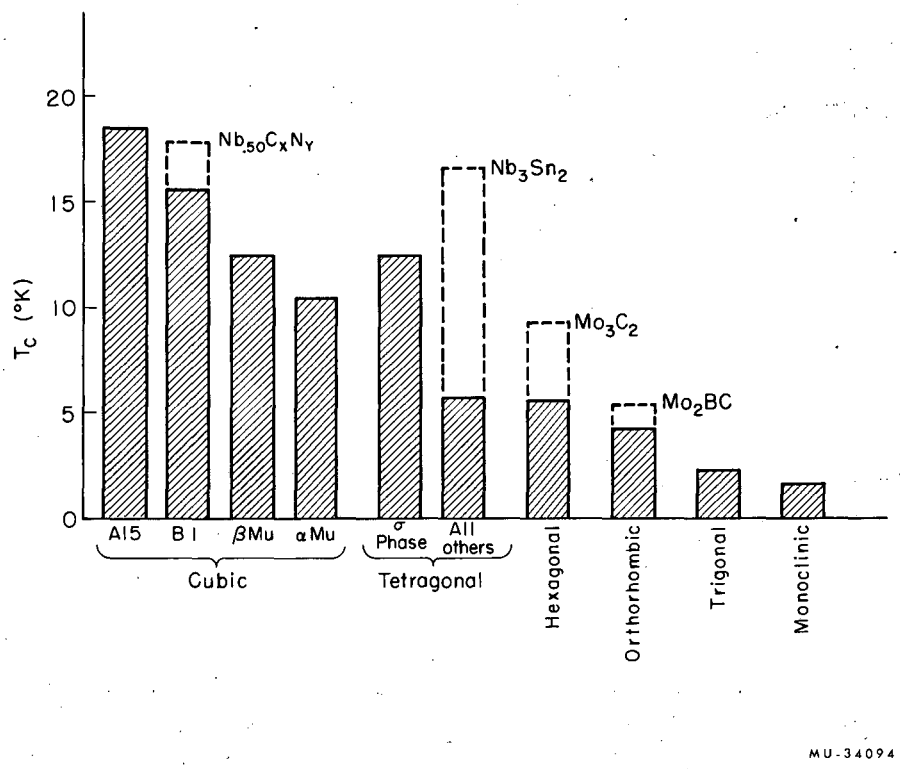
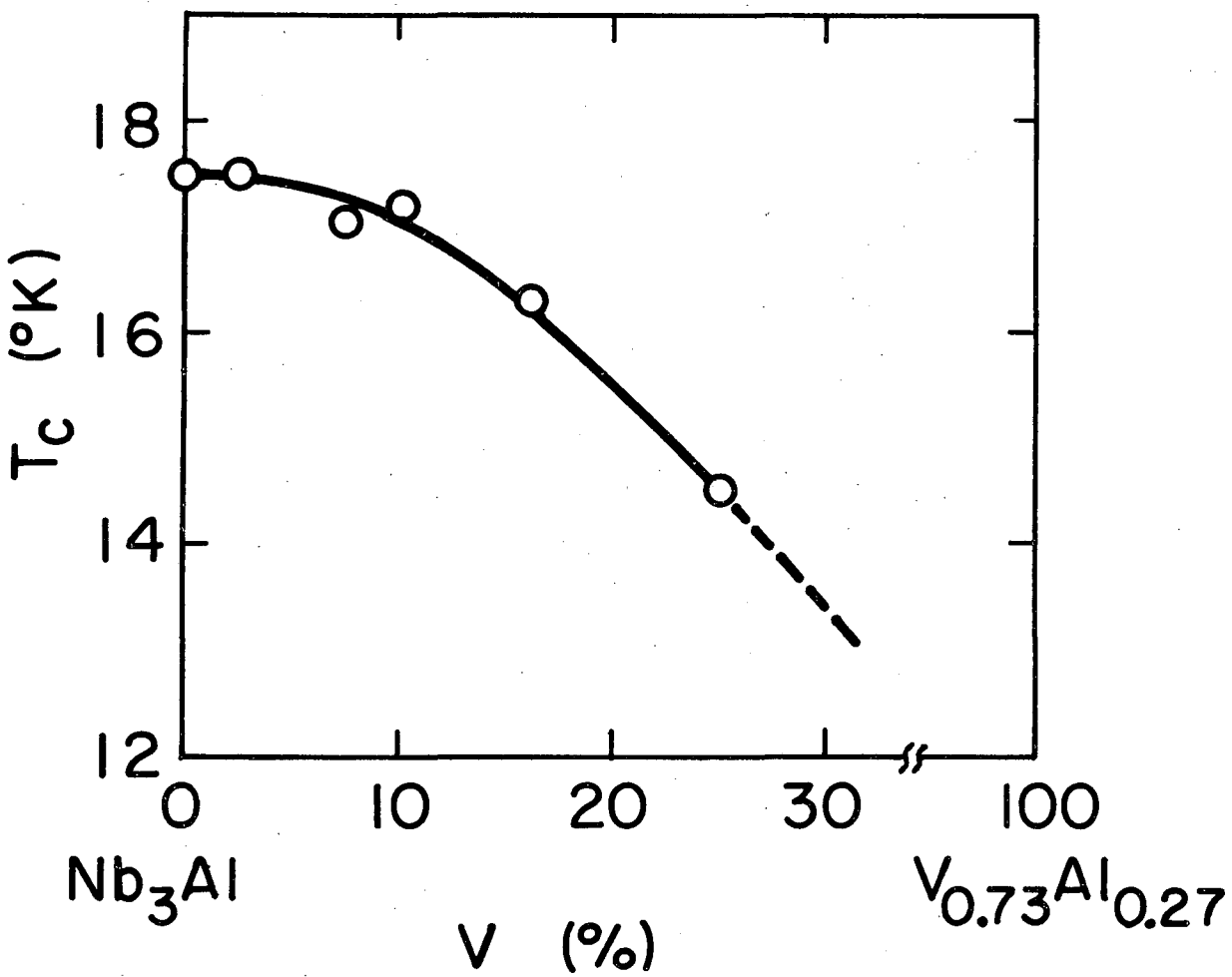
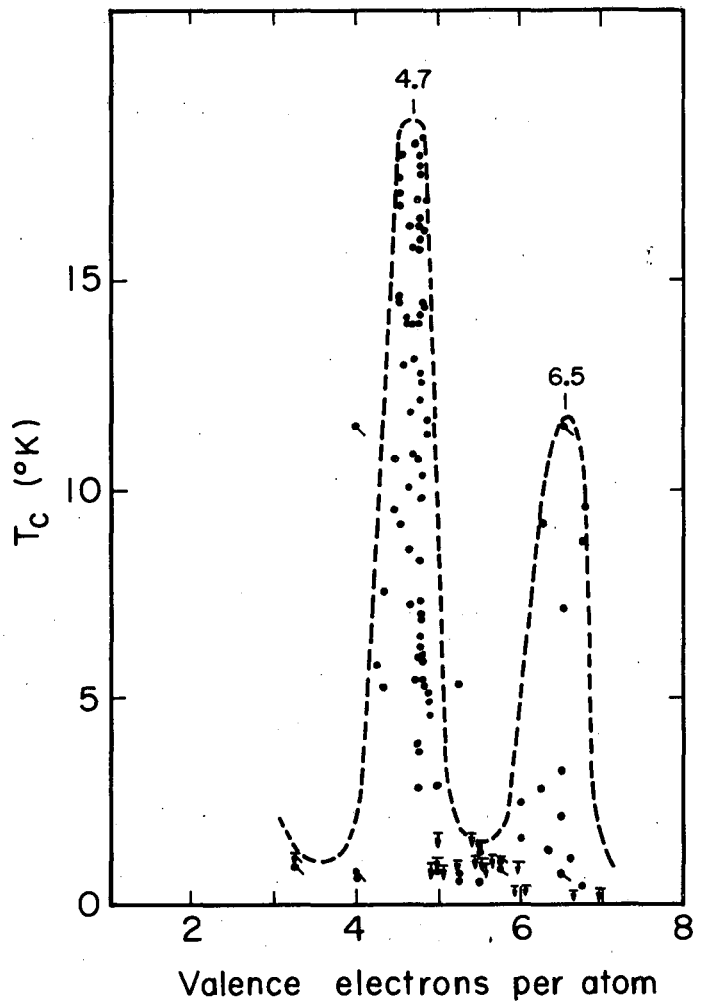


Fig. 5. Correlation of transition temperature, T_c, with crystal structure showing a decrease of T_c with decrease in symmetry.



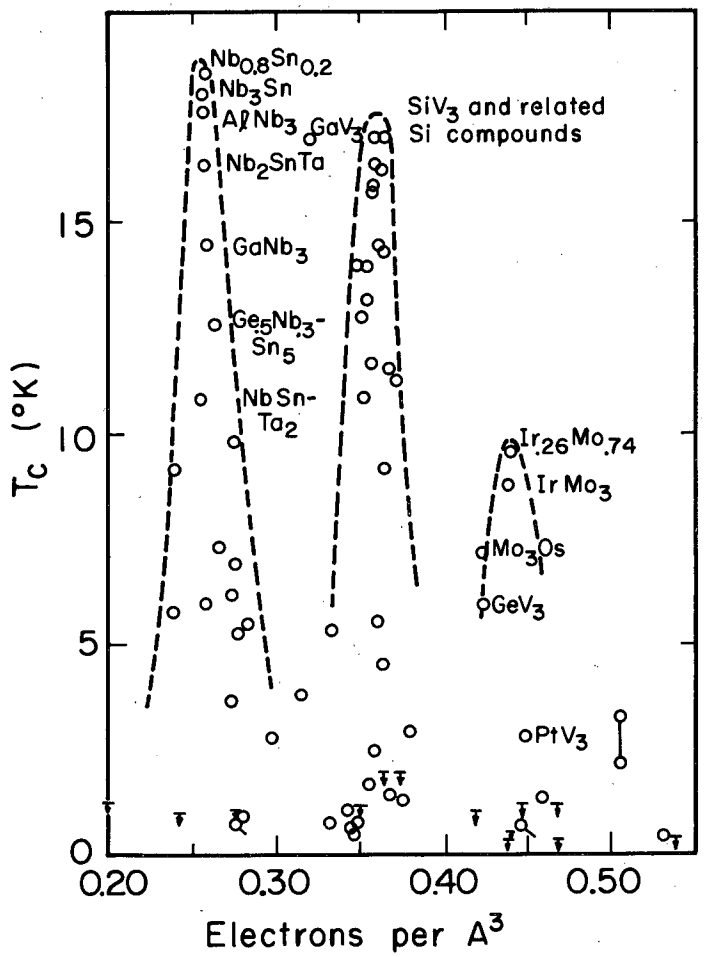
MUB-2798

Fig. 6. Variation of transition temperature (T_c) with addition of vanadium for the A15 compound Nb_3Al.



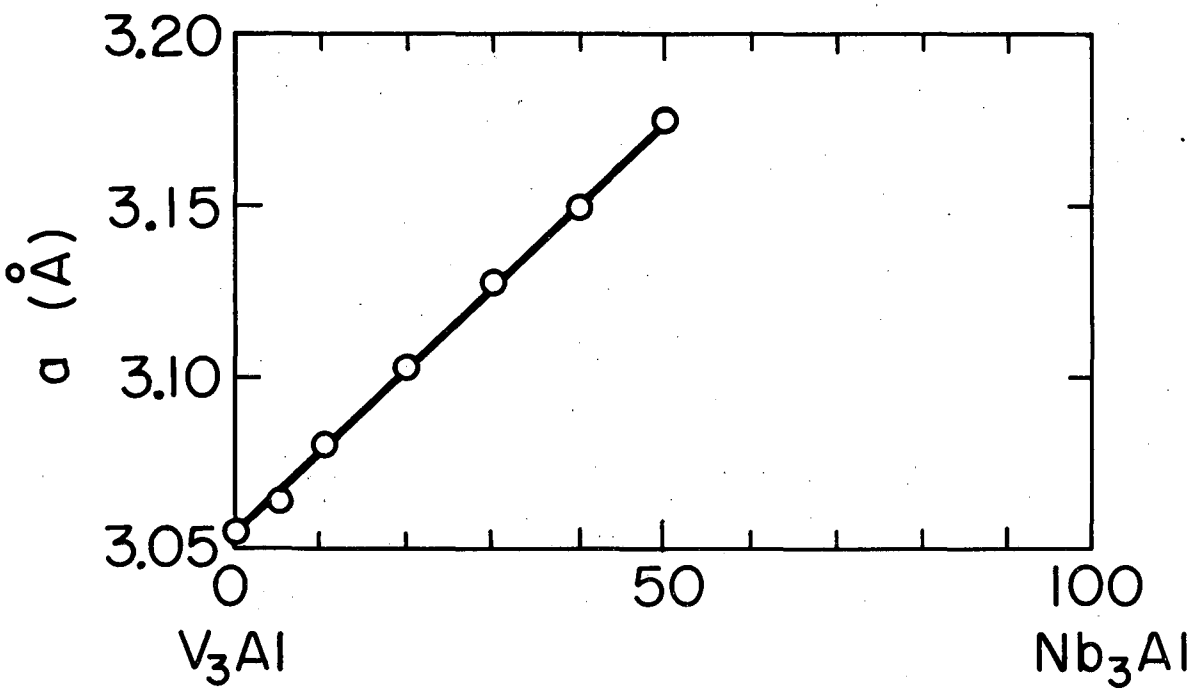
MU-34052

Fig. 7. Critical temperature dependence on average number of valence electrons per atom for A15 (β-W)-type compounds.[18]



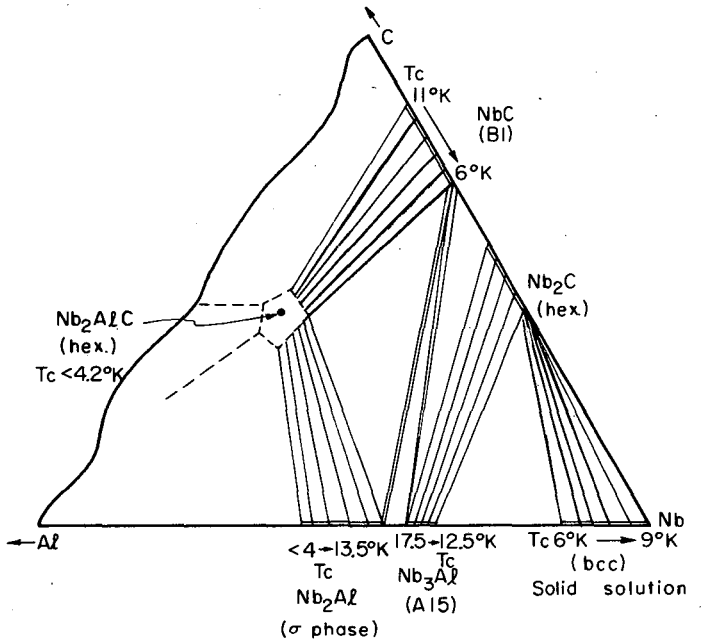
MU-34053

Fig. 8. Critical temperature as a function of electron density for A15 (β-W)-type compounds. (Note: Dashed lines represent apparent envelopes of experimental points only.)[18]



MUB-2799

Fig. 9. Variation of lattice parameter with addition of niobium for the bcc solid solution $V_{0.73}Al_{0.27}$.



MU-34095

Fig. 10. Equilibrium diagram for the Nb-rich corner of the Nb-Al-C ternary system showing phases present and T_c data obtained.

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