

# Lawrence Berkeley National Laboratory

## Recent Work

### Title

SOME SUPERCONDUCTING PROPERTIES OF SEVERAL CARBIDES AND NITRIDES OF THE TRANSITION METALS

### Permalink

<https://escholarship.org/uc/item/86r508h6>

### Authors

Toth, L.E.  
Zackay, V.F.  
Johnston, J.  
et al.

### Publication Date

1964-07-01

# University of California

## Ernest O. Lawrence Radiation Laboratory

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy  
which may be borrowed for two weeks.  
For a personal retention copy, call  
Tech. Info. Division, Ext. 5545*

SOME SUPERCONDUCTING PROPERTIES OF SEVERAL  
CARBIDES AND NITRIDES OF THE TRANSITION METALS

Berkeley, California

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

UNIVERSITY OF CALIFORNIA  
Lawrence Radiation Laboratory  
Berkeley, California

Contract No. W-7405-eng-48

SOME SUPERCONDUCTING PROPERTIES OF SEVERAL  
CARBIDES AND NITRIDES OF THE TRANSITION METALS

L. E. Toth, V. F. Zackay, J. Johnston, M. Wells, and E. R. Parker

July 1964

SOME SUPERCONDUCTING PROPERTIES OF SEVERAL  
CARBIDES AND NITRIDES OF THE TRANSITION METALS

L. E. Toth,<sup>\*</sup> V. F. Zackay, J. Johnston, M. Wells, and E. R. Parker

Inorganic Materials Research Division, Lawrence Radiation Laboratory  
and Department of Mineral Technology, College of Engineering  
University of California, Berkeley, California

Abstract

Analogous to the transition elements, their solid solutions, and intermetallic compounds, a correlation is shown to exist between the total number of valence electrons and the superconducting critical temperature for transition metal carbides and nitrides crystallizing in the NaCl structure. The critical temperature increases as the total number of valence electrons increases from eight to about ten. A number of experiments were undertaken to substantiate the correlation. The critical temperature of cubic molybdenum carbide (NaCl structure) was found to be 13.0°K. The critical temperature of the two-phase mixtures of cubic and hexagonal molybdenum carbide was found to be dependent upon the relative amounts of the two phases present. This behavior was tentatively explained on the basis of the structural similarities of the two phases. A critical temperature for the hypothetical compound, cubic TaN, of 12°-14°K is predicted from the variation of the critical temperature with composition for the cubic solid solutions of TaN and TaC.

---

\* Presently at the Department of Metallurgy, University of Minnesota, Minneapolis, Minnesota.

## INTRODUCTION

The existence of maxima in the superconducting transition critical temperatures at the approximate electron-to-atom ratios of 4.7 and 6.5 has been substantiated by a number of workers<sup>(1,2,3)</sup> for a variety of elements, solid solutions, and intermetallic compounds. This paper relates to analogous studies in the relationship of the critical temperature to the electron-to-atom ratio in metal-nonmetal compounds such as the nitrides and carbides. Matthias and Hulm<sup>(4)</sup> have suggested that studies of this kind should be restricted preferably to a particular crystal structure. In conformance with this suggestion, we have chosen to study the superconducting properties of compounds crystallizing in the NaCl structure. As is well known, a large number of metal carbide and nitride compounds crystallize in this structure.

In the present series of investigations, a correlation between a maximum in the critical temperature and the total number of valence electrons in the compound was found. The correlation applied equally well to both the carbides and nitrides of the transition elements. In the course of the experimental phase of this study, it was found that the critical temperature of multiphase MoC (cubic and hexagonal) was related to the proportions of each phase present.

Because of experimental difficulties in preparing the carbides and nitrides, the early literature on their superconducting behavior contains numerous examples of widely different values for the reported transition temperature. The strong dependence of the critical temperature upon the deviation from stoichiometry has caused, in the past, a great deal of confusion. The mono-carbides and mono-nitrides exist over a wide range of compositions; tantalum carbide, for example, is known to exist from  $TaC_{0.99}$  to  $TaC_{0.75}$ .<sup>(5)</sup> In a careful investigation of the variation of  $T_c$  with carbon content,

Giorgi et al.<sup>(5)</sup> found that the critical temperatures decreased from 9.7°K to less than 1.0°K as the carbon content decreased from 0.99 to 0.75 (see Fig. 1). In general, the  $T_c$  of these mono-carbides and mono-nitrides is highest as the stoichiometric 1:1 ratio is approached.

Although the carbides, nitrides, borides, and silicides of the transition elements are often grouped together as one broad class, there is crystal-chemical evidence that the carbides and nitrides form a group distinct from the other two. Most of the transition metals of the left side of the periodic table form mono-carbides and mono-nitrides with the NaCl structure. The complete solid solubility that exists between the carbides and nitrides within the limits of volume restrictions or changes of crystal structure suggests that the electronic structure of the carbides and nitrides are similar. This similarity does not extend to other refractory materials such as the borides or silicides, which crystallize in structures different from those of carbides and nitrides. Little solid solubility exists, for example, between the carbides and borides.<sup>(6)</sup> This distinction between the carbides, nitrides, and borides has also been suggested by Alekseevski et al.<sup>(7)</sup> who have stressed the importance of metal-to-nonmetal bonds in the carbides and nitrides. Nonmetal-nonmetal interactions do not occur in the carbides and nitrides with the NaCl structure but do occur in the borides, as exemplified by the formation of the well-known boron chains or layers.

Treating the cubic carbides and nitrides as one class of compounds, a close relationship in their critical temperatures can be found. We observed on the basis of a literature survey of the existing  $T_c$  values that the critical temperatures of the carbides of the IV (Ti, Zr, Hf), V (V, Nb, Ta) or VI (Cr, Mo, W) group transition metals were nearly the same as those of the nitrides of the preceding group.<sup>(8)</sup> For example, the critical

temperature of NbC is nearly the same as that of ZrN. The critical temperature depends upon the total number of valence electrons, i.e., the sum of both the metallic and nonmetallic elements. Here, the number of valence electrons means all the electrons beyond a closed shell. The critical temperatures of the carbides and nitrides with 8, 9, and 10 total valence electrons are shown in Table I. The latest values of critical temperatures were taken from the literature. The ones selected were for those compositions closest to stoichiometry. In view of the strong dependence of  $T_c$  on the deviation from stoichiometry, these critical temperatures should be compared with compounds with identical metal-to-nonmetal ratios. Unfortunately, in most cases, the exact composition of the compound was not reported, thus making such an ideal comparison impossible.

The table is arranged to place the nitrides of the third group metals next to the carbides of the fourth group metals, etc., and also arranged according to the row in the periodic table of the transition metal. All of the compounds with 8 total electrons are normal (i.e., not found to be superconducting above about 1°K) for both the carbides and nitrides. All of the interstitial compounds with 9 or 10 total electrons are superconducting with the exception of VC. This compound cannot be prepared stoichiometrically, however, and the composition  $VC_{0.88}$  contains only 8.5 total electrons.

To substantiate the correlation between the nitrides and carbides, a number of experiments were undertaken. As may be seen in Table I, the maximum critical temperature of a binary compound is found for NbN with 10 total electrons. If the present interpretation of the band structure



Table I

Superconducting Properties of the Carbides and Nitrides with the NaCl Structure\*

Group III nitrides			Group IV carbides		
Compound	Total valence electrons at stoichiometry	Critical Temperature	Compound	Total valence electrons at stoichiometry	Critical Temperature
ScN	8	Normal**	TiC	8	Normal
YN	8	Not known	ZrC	8	Normal
LaN	8	Normal	HfC	8	Normal
Group IV nitrides			Group V carbides		
TiN	9	5.6°K	VC***	9	Normal
ZrN	9	10.7°K	NbC	9	11.1°K
HfN	9	6.2°K	TaC	9	9.7°K
Group V nitrides			Group VI carbides		
VN	10	8.2°K	CrC	10	Does not exist with NaCl structure
NbN	10	15.8°K	MoC	10	Present series of investigations
TaN	10	Present series of investigations	WC	10	Exists at high temperatures only

\* Values quoted are those listed by Roberts<sup>(9)</sup> and Matthias et al.<sup>(10)</sup>

\*\* "Normal" means not superconducting at about 1°K. Consult Roberts<sup>(9)</sup> or Matthias et al.<sup>(10)</sup> for the exact temperatures.

\*\*\* VC<sub>0.88</sub> is the highest carbon ratio which can be obtained by usual techniques; this composition corresponds to 8.5 electrons.

of these compounds is correct, we would expect that other carbides and nitrides with 10 or nearly 10 total electrons would have critical temperatures nearly equal to that of NbN. The carbides and nitrides that have not been tested for superconductivity and which would have 10 electrons are TaN and the fourth group carbides. Unfortunately, these compounds either do not crystallize in the NaCl structure (TaN and CrC) or crystallize in the NaCl structure only at very high temperatures (MoC and WC). In the latter case, the transformation from the NaCl structure to the lower temperature phase occurs at an extremely rapid rate. In order to retain the cubic phase, a drastic quenching technique had to be developed which was then employed to retain the cubic phase of MoC but failed in the case of WC. In order to obtain information about the critical temperature of TaN, a solid solution of the cubic phase between TaC and TaN was formed. The latter method is, however, not applicable to CrC or WC, as these compounds form only limited solid solubility ranges with the fifth group carbides that possess the NaCl structure.

## EXPERIMENTAL

### I. MoC

A high temperature phase at the approximate composition MoC, with a hexagonal unit cell, has been known to exist for some time. Only recently the cubic modification (NaCl) has been found. In a series of papers by Rudy et al. (6,11) and independently by Clougherty et al., (12) it was reported that the cubic  $\alpha$ -MoC crystallizes from the molten state at about 2600°C. At approximately 2200°C cubic  $\alpha$ -MoC transforms very rapidly into the related hexagonal phase,  $\eta$ -MoC. The composition of this hexagonal phase is believed to be at the composition corresponding to the formula MoC<sub>0.67</sub> and not at MoC.

Because the transformation from the cubic to the hexagonal form occurs very rapidly, drastic quenches are needed to retain the cubic phase at room temperature and even then it has never been obtained in a completely pure form.

In the present series of investigations a series of hot-pressed samples in the Mo-C binary system were quenched (from graphite crucibles) from five different temperatures, 1650, 2200, 2320, 2415, and 2650°C into liquid tin or into oil. (8) The results of x-ray analysis and critical temperature measurements are shown in Table II. The samples quenched from 1650°C showed only the hexagonal  $\eta$ -MoC, the samples from 2200°C were mainly  $\eta$ -MoC but had partially transformed to cubic  $\alpha$ -MoC, while the samples quenched from higher temperatures were mainly cubic  $\alpha$ -MoC.

The critical temperature of the cubic molybdenum carbide quenched from 2415°C in Sn was 13.0°K with the transition extending from 13.5°K to 12.5°K. Little variation could be detected in  $T_c$  with a change in composition; the lack of sensitivity of  $T_c$  to composition changes is merely a reflection of the fact that cubic  $\alpha$ -MoC phase exists only over a small range of composition. The limited range of composition variation for the existence of this phase is related to its limited stability. The cubic form is always defective in carbon content and probably does not exist beyond the composition  $\text{MoC}_{0.80}$ . The composition limits on this phase are presently being determined.

The desired compound was cubic MoC with a total of ten valence electrons. The nominal composition of the phase actually obtained was  $\text{MoC}_{0.8}$  with a total of 9.2 valence electrons. The high critical temperatures (13°K) is surprising in view of the large deviation from stoichiometry. For example, the critical temperature of  $\text{NbC}_{.8}$  is less than a degree while that of  $\text{NbC}_{.97}$  is about 11°K. (5)

The critical temperature of the pure hexagonal  $\eta$ -MoC quenched from 1650°C was 9.0°K. This temperature is nearly the same as the 9.26°K reported by

Table II

Selected Values of X-Ray Findings and Critical Temperatures in the Mo-C Binary Systems

Sample No.	Nominal composition		Phase	Temperature of Quench °C	Critical temperature at middle of transition °K	Width of transition °K
	Mo	C				
1	60	40	Hexagonal MoC	1650 (Tin)	9.0	0.4
2	60	40	Hexagonal + Cubic	2200 (Tin)	11.0	0.5 (?)
3	59	41	Cubic + Trace hexagonal	2320 (Tin)	12.0	1.2
4	56	44	Cubic + Trace hexagonal	2415 (Tin)	13.0	1.0
5	60	40	Cubic + Trace hexagonal	2650 (Oil)	12.2	2.9

Matthias and Hulm<sup>(4)</sup> for arc-melted specimens. The specimens quenched from 2200°C into tin had critical temperature varying from 9.5 to 11.0°K. These temperatures are intermediate between those for the pure cubic phase and the pure hexagonal phase. X-ray analysis showed that the critical temperature increased with increasing amount of NaCl structure.

## II. TaN

Tantalum nitride crystallizes in a hexagonal structure; this phase has not been found to be superconducting at 1.28°K. In an attempt to determine the critical temperature of TaN with the NaCl crystal structure, a solid solution between TaC and TaN was formed. Compacted mixtures of the powders of TaC and TaN were reacted under 1 atm of nitrogen pressure. Chemical analysis was used to determine the resultant composition. The NaCl structure was found to exist in solid solutions of Ta(C,N) to about 38 mole percent TaN.

Shown in Fig. 2 are the median temperatures of the superconducting transition temperatures and a linear extrapolated value of about 13.7°K for the  $T_c$  of pure TaN. The extrapolation is crude since it extends over 60 mole percent. Furthermore, the extrapolation is linear and there is no a priori assurance that the variation should remain linear, particularly near the TaN side of the phase diagram. A linear variation is found, however, in a number of pseudo binary systems such as the ZrN-HfN system.<sup>(13)</sup> In addition to the linear variation, another common type of variation is a maximum in  $T_c$ .

In the solid solutions NbC and TaC, a pronounced maximum in  $T_c$  was found at about 60 mole percent NbC.<sup>(14)</sup> Matthias<sup>(15)</sup> has suggested that this maximum results from a gradual variation in the deviation from stoichiometry. Another maximum in critical temperatures occurs in solid solutions of NbC and NbN in which a maximum value for  $T_c$  of 17.8°K was found at 80 mole percent NbN. This maximum occurs at the electron-to-atom ratio of 4.85 which is near

the optimum value for high  $T_c$ 's in the transition metals. Since tantalum and niobium are in the same group in the periodic table, a similar maximum might also occur in the TaC-TaN pseudo binary system. The dotted curve for the maximum in critical temperature shown in Fig. 2 was drawn assuming a similar variation to that found in the NbC-NbN systems. The critical temperature for cubic TaN is thus estimated to lie between the end points of the two curves, i.e., 12 and 14°K.

## DISCUSSION

### I. Correlation

The experiments on MoC and TaN substantiate the proposed correlation of the superconducting properties of the carbides and nitrides. The critical temperature of MoC is the highest known transition temperature for any binary carbide and nearly equal to that of NbN. The substitution of nitrogen for carbon in TaC increased  $T_c$  as expected on the basis of the proposed correlation. The superconducting transition temperatures of the fifth group nitrides and the sixth group carbides with the NaCl structure are higher than those of the nitrides and carbides of the preceding groups. It would be of value to obtain the cubic form of WC and obtain its superconducting properties. Attempts to do so are being continued by one of the authors (L.T.).

It is interesting to see whether the present correlation is consistent with the theoretical models proposed to explain the electrical properties of these compounds. In general, the bonding models fall into two classes, those in which the interstitials act as electron donors to the d-band of the transition metal, (Dempsey)<sup>(16)</sup> and those in which the interstitial is electronically neutral but is engaged in strong metal-to-nonmetal bonding (Billz)<sup>(17)</sup>

Dempsey<sup>(16)</sup> has proposed that the interstitial atoms contribute their p-electrons to the d shell of the transition element and that the band

structure is not drastically altered by the presence of the interstitial atoms. Carbon would contribute two electrons and nitrogen three electrons to the d-band of the transition metal. Thus, carbon would have a positive charge of two and nitrogen of three. The density of states curve for the carbides and nitrides would resemble that found for the transition metals, with nearly equally sized peaks in the density of states about the midpoint in the d-bands at 5 electrons.

A number of investigators, however, have stressed the importance of the metal-to-nonmetal bonding.<sup>(17,18,19)</sup> Bilz<sup>(17)</sup> has assumed that there is bonding between the s-p hybrid orbital of the interstitial and the spd hybrid orbitals of the transition metal. On the basis of a tight-binding calculation, he obtained a theoretical model for the variation in the density of states with energy. The bonding p-bands are separated by a low density of states band from the d-bands. The Fermi level for carbides and nitrides with 8 valence electrons, TiC, for example, lies near the minimum in the density of states while for carbides and nitrides with 9 valence electrons it lies in the d band with its corresponding larger density of states.

Qualitatively, the band models proposed by Bilz and Dempsey are similar in that they both have a minimum in the density of states. As seen from Fig. 3, the density of states in the Dempsey model would be symmetric about this minimum. In contrast, the density of states would be asymmetric about the minimum in the Bilz model. In both models the minimum would occur at nearly the same number of total electrons. Since the superconducting transition temperature depends exponentially on the density of states at the Fermi surface, the known critical temperatures can be used to indicate the qualitative behavior of the density of states. The critical temperatures indicate that there is a minimum in the density of states at 8 electrons and that it

increases with increasing number of total electrons. Indeed, the qualitative variation in the density of states obtained from the total is very nearly the same as proposed by Bilz or Dempsey. As can be seen from Fig. 3, the compounds treated in the present correlation are all on the right side of the minimum and here the two models are qualitatively identical. We conclude that the present correlation agrees with both models but that it cannot be used to distinguish between them.

## II. The Influence of Crystal Structure on the $T_c$ of Hexagonal and Cubic Molybdenum Carbide

During the experiments on MoC an unusual dependence of  $T_c$  on quenching temperature was observed. It was found that the critical temperatures of samples containing nearly equal amounts of the cubic and hexagonal forms of MoC were intermediate between the critical temperature of the pure hexagonal 9.0°K and that of the nearly pure cubic phase, 13.0°K. We believe that these intermediate critical temperatures can be explained on the basis of the transformation that occurs in the phase change.

As Matthias and Hulm<sup>(4)</sup> pointed out, the hexagonal crystal structure is not as favorable as is the cubic structure for the occurrence of high  $T_c$ 's in these refractory compounds. The probable explanation of the high  $T_c$  for hexagonal  $\eta$  phase is that its crystal structure is very closely related to that of the cubic phase. Nowotny et al.<sup>(20)</sup> have found that this hexagonal phase belongs to the  $D_{6h}^4$  space group with an ABCACB, ABCACB sequential ordering of the atomic planes of the Mo atoms. This unit cell contains a subcell with the NaCl sequential ordering ABC, ABC. The hexagonal unit cell is just two NaCl unit cells placed on top of one another in an inverted order.

Because of the geometric similarities in the crystal structure between the hexagonal and cubic phase, the transformation is one involving only a change in the sequential ordering of the molybdenum close packed layers.



It is possible that during the transformation the sequential ordering of the layers of metallic atoms would vary between cubic and hexagonal. If the transformation occurs on an atomic level or over distances small compared to the mean free path, the electronic changes would average over the structural changes. Consistent with this suggestion, the critical temperature appeared to be related to the relative proportions of cubic and hexagonal phases present. We believe that this is the first observation of a gradual change in  $T_c$  dependent upon the amount of each phase present. An analogous phenomenon has been observed by a number of investigators<sup>(21,22,23)</sup> using thin film composites of normal and superconducting materials.

### III. Magnetic Measurements

The high normal resistivity and the high critical temperatures of the carbides and nitrides make them promising materials for high critical magnetic fields. Magnetic measurements are presently being undertaken in conjunction with Drs. H. J. Fink and A. C. Thorsen and their associates at Atomics International, Canoga Park, California. Preliminary results on MoC confirm the expectation that MoC is a high field type II superconductor.

### SUMMARY

Matthias and others have shown definite correlations between the occurrence of superconductivity and the electron-to-atom ratio of transition elements, solid solutions, and intermetallic compounds.

The authors of the present paper show that an analogous correlation exists between the total number of valence electrons and the occurrence of superconductivity for transition metal carbides and nitrides crystallizing in the NaCl structure. Several experiments are suggested from this correlation regarding the existence of new high critical temperature superconductors.

The critical temperature of metal-nonmetal compounds is shown to increase with increasing total number of valence electrons. The critical temperature

appears to be a maximum for a total of about ten valence electrons. Consistent with these indicated trends, the critical temperature of a transition metal nitride is greater than its carbide.

The cubic modification of molybdenum carbide obtained by suppression of the equilibrium hexagonal phase through drastic quenching, is found to be superconducting with a critical temperature of 13°K. The high critical temperature of this compound was predicted on the basis of its having a favorable number of total valence electrons.

The critical temperature for cubic TaN is estimated to be between 12 and 14°K. The predicted high critical temperature for cubic TaN is also consistent with the correlation of critical temperature with total valence electrons.

The present qualitative correlation between the total number of valence electrons and the critical temperature is not inconsistent with either the band models of Bilz and Dempsey.

The critical temperature of two-phase mixtures of hexagonal and cubic  $\text{MoC}_{1-x}$  was dependent upon the relative amounts of the two phases present. This behavior can be tentatively explained on the basis of the similarities of the crystal structures of the two phases. For this explanation to be valid, it is necessary to assume that the mean free path of paired superconducting electrons be greater than the distance between the average width of either phase. Thus, the possibility exists that the critical temperature, a relatively simple measurement, can be used to yield information about the structure of superconducting materials.

Preliminary results on MoC confirm the expectation that MoC is a high field type II superconductor.

Acknowledgments

The authors gratefully acknowledge helpful discussions with Professors J. Friedel, Universite de Paris; L. Brewer and J. Garland, University of California, Berkeley; Dr. E. Rudy, Aerojet-General, Sacramento; Dr. M. Pickus and Mr. K. Kennedy, University of California, Berkeley. This work was performed under the auspices of the U. S. Atomic Energy Commission through the Inorganic Materials Research Division of the Lawrence Radiation Laboratory.

References

1. B. T. Matthias, Phys. Rev., 92, 874 (1953).
2. J. K. Hulm and R. D. Blaugher, Phys. Rev., 123, 1569 (1961).
3. B. W. Roberts, "Superconductive Intermetallic Compounds," G. E. Research Laboratory Report No. 64-RL-3540M (January 1964).
4. B. T. Matthias and J. K. Hulm, Phys. Rev., 87, 798 (1952).
5. A. L. Giorgi, E. G. Szklarz, E. K. Storms, A. L. Bowman and B. T. Matthias, Phys. Rev., 125, 837 (1962).
6. See for example, E. Rudy, F. Benesovsky and L. E. Toth, Zeit. f. Metallk., 54, 345 (1963).
7. M. E. Alekseevski, G. V. Samsanov and O. J. Shulitsova, J. Exp. Theor. Phys., 44, 1413 (1963).
8. L. E. Toth, E. Rudy, J. Johnston and E. R. Parker, submitted for publication in the J. Phys. and Chem. of Solids.
9. B. W. Roberts, "Superconductive Materials and Some of Their Properties," G. E. Research Lab. Report No. 63-RL-3252M (March 1963).
10. B. T. Matthias, T. H. Geballe and V. B. Compton, Rev. of Phys., 35, 1 (1963).
11. E. Rudy, El. Rudy and F. Benesovsky, Planerber. Pulvermetallurgie, 10, 42 (1962).
12. E. V. Clougherty, K. H. Lothrop and J. A. Kafalas, Nature, 191, 1194 (1961).
13. A. L. Giorgi and E. G. Szklarz, Bull. Am. Phys. Soc., 7, 176 (1962).
14. M. Wells, M. Pickus, K. Kennedy and V. Zackay, Phys. Rev. Letters, 12, 536 (1964).
15. B. T. Matthias, private communication.
16. E. Dempsey, Phil. Mag., 8, 285 (1963).
17. H. Bilz, Z. Physik., 153, 338 (1958).
18. R. E. Rundle, Acta Cryst., 1, 180 (1948).
19. H. Krebs, Acta Cryst., 2, 95 (1956).
20. H. Nowotny, E. Parthe, R. Kieffer and F. Benesovsky, Mh. Chem., 85, 255 (1954).

21. P. G. De Gennes, Reviews of Modern Physics, Jan. 1964, p. 225.
22. N. R. Werthamer, Physical Review, 132, 6, (1963).
23. P. Hilsch, Z. Physik, 167, 511 (1962).

Figure Captions

Fig. 1 The variation in the  $T_c$  of  $NbC_{1-x}$  and  $TaC_{1-x}$  with carbon content (after Giorgi et al.)<sup>(5)</sup>

Fig. 2 The variation in  $T_c$  with composition in the TaC-TaN pseudo-binary system. The dotted line is a linear extrapolation to cubic TaN. The second dotted line corresponds to a variation of  $T_c$  with composition as found in the NbN-NbC system.

Fig. 3(a) The variation in the density of states with energy according to Bilz<sup>(17)</sup> for the carbides and nitrides with the NaCl structure. Here  $\Sigma$  refers to the sum of the valence electrons of the metal and nonmetal atoms.

3(b) The qualitative variation in the density of states as expected from the Dempsey<sup>(16)</sup> model. The shaded area in both figures refers to the region dealt with in the present correlation.

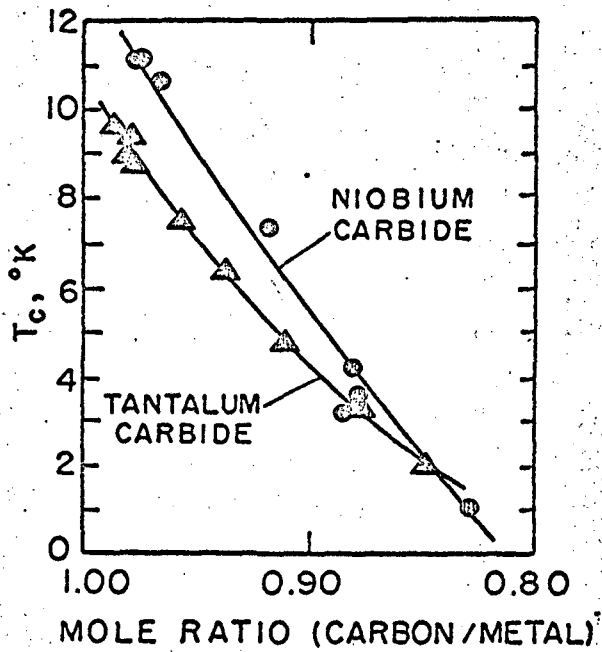


Fig. 1

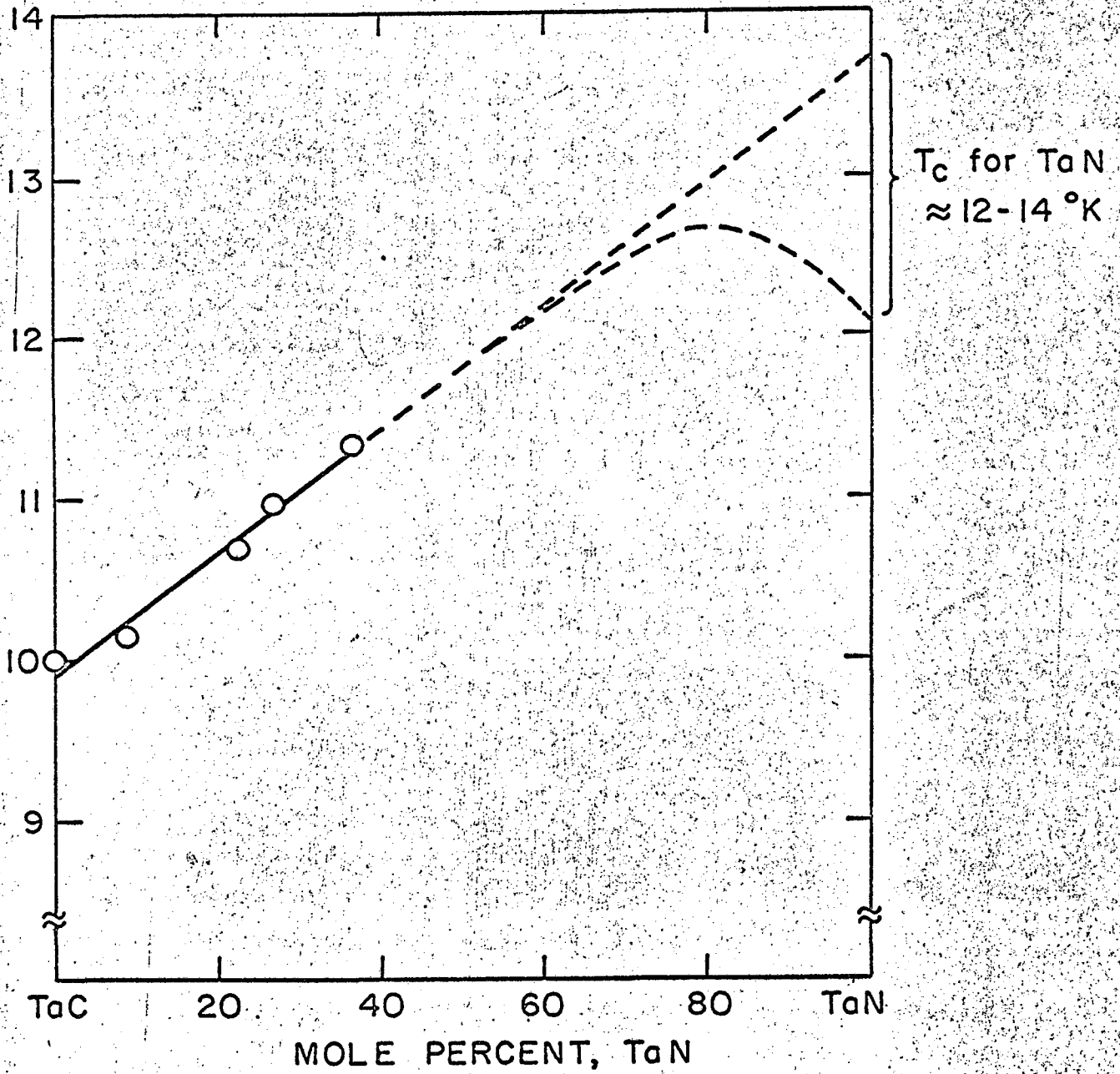


Fig. 2



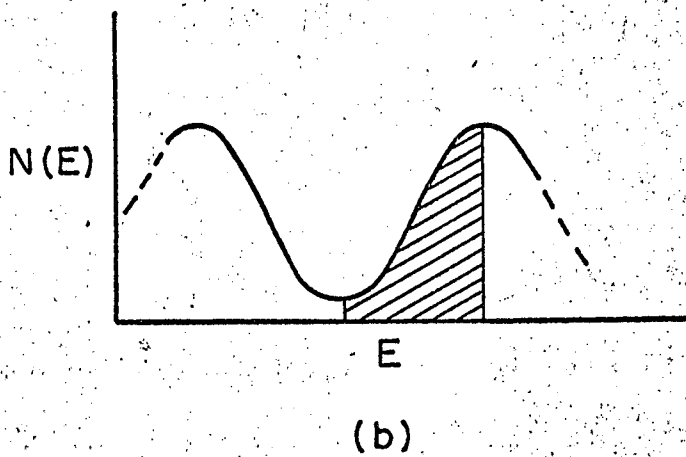
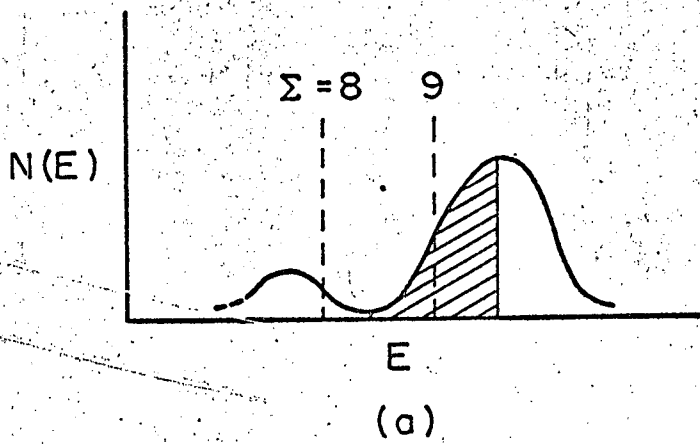


Fig. 3

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

