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

**Berkeley, California**

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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

## 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 investigation, 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. This is thought to be due to the geometrical similarities of the crystal structures.

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. Literature values for the transition temperature of NbN with NaCl structure vary from 23°K<sup>(5)</sup> to 9°K,<sup>(6)</sup> the upper limit undoubtedly

resulting from the use of the resistance technique of measuring the appearance of superconductivity. Tantalum carbide, as another example, was reported to be superconducting at  $9.2^{\circ}\text{K}$ ,<sup>(7)</sup> later found not to be superconducting above  $1.2^{\circ}\text{K}$ .<sup>(8,9)</sup> The discrepancy in this case resulted from a variation in the carbon content of the mono-carbide. The mono-carbides and mono-nitrides exist over a wide range of compositions; tantalum carbide, for example, is known to exist from  $\text{TaC}_{0.99}$  to  $\text{TaC}_{0.75}$ .<sup>(10)</sup> In a careful investigation of the variation of  $T_c$  with carbon content, Giorgi et al.<sup>(10)</sup> found that the critical temperatures decreased from  $9.7^{\circ}\text{K}$  to less than  $1.0^{\circ}\text{K}$  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.

In contrast to intermetallic compounds with the  $\beta$ -tungsten crystal structure, ternary additions or substitutions into the NaCl lattice of the carbides and nitrides often cause an increase in  $T_c$ . Matthias,<sup>(1)</sup> for example, observed that in a solid solution between NbC and NbN the critical temperature of the NaCl phase went through a maximum of  $17.8^{\circ}\text{K}$ . Wells et al.<sup>(11)</sup> found a similar maximum in samples in the solid solution between NbC and TaC (see Fig. 2). No complete explanation has yet been found for these maxima. The maximum  $T_c$  in solid solutions between NbC and TaC is interesting since niobium and tantalum belong to the same group in the periodic table, and so this maximum cannot be explained by a variation in the electron to atom ratio. Matthias<sup>(12)</sup> has suggested that a possible explanation for this particular maximum is a variation in the carbon content as shown in Fig. 3. The critical temperature for  $\text{NbC}_{0.98}$  is  $13.2^{\circ}\text{K}$ , for  $\text{TaC}_{0.98}$  it is  $9.0^{\circ}\text{K}$  and for  $\text{NbC}_{0.96}$  it is  $10.3^{\circ}\text{K}$ .<sup>(12)</sup>

The carbon deficiency of NbC is twice that of the TaC. In the solid solution there will be an intermediate carbon deficiency which would result in a non-linear behavior of  $T_c$  such as the dotted curve shown in Fig. 3 which is intermediate between the two solid lines.

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 suggest 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 crystallise in structures different from those of carbides and nitrides. Little solid solubility exists, for example, between the carbides and borides. (13)

This distinction between the carbides-nitrides and borides has also been suggested by Alekseevski et al. (14) who have stressed the importance of metal-to-non-metal bonds in the carbides and nitrides. They have observed that the transition temperature increases as the amount of metal-to-non-metal type of bonding increases as, for example, when stoichiometry of the mono-carbides and mono-nitrides is approached. Metal-to-non-metal bonding probably occurs in the NaCl structure since each non-metal is surrounded by 6 metal atoms and has no other non-metal atoms for closest neighbors. In the borides, however, localized interactions between the boron atoms occur, as exemplified by the formation of the well-known boron chains or layers.

Treating the carbides and nitrides with the NaCl structure as one class of compounds, a close relationship in their critical temperatures

can be found. Toth et al.<sup>(15)</sup> observed 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. The critical temperature depended on the total number of valence electrons, the sum of both the metallic and non-metallic elements. The critical temperatures of the carbides and nitrides with 8, 9, 10 total valence electrons are shown in Table I. 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 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<sub>0.88</sub> contains only 8.5 total electrons. The highest T<sub>c</sub> is for NbN with 10 total valence electrons. In general, the carbides and nitrides with the same number of valence electrons have nearly the same critical temperature.

The observed critical temperatures of the nitrides and carbides with the NaCl structure may be understood with the aid of the tight-binding calculations of Bilz.<sup>(18)</sup> In this model, the hardness, brittleness, and high melting temperatures of these compounds result from the formation of strong metal-to-non-metal bonds, the importance of these strong metal-to-non-metal bonds had been first suggested by Rundle<sup>(19)</sup> and Krebs.<sup>(20)</sup> On the basis of a tight-binding calculation, Bilz<sup>(18)</sup> has found that the

Table I

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

Group III nitrides			Group IV carbides		
Compound	Total valence electrons	Critical Temperature	Compound	Total valence electrons	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***	8.5	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	13.0°K
TaN	10	Does not exist with NaCl structure	WC	10	Exists at high temperatures only

\* Values quoted are those listed by Roberts<sup>16</sup> and Matthias et al.<sup>17</sup>

\*\* "Normal" means not superconducting at about 1°K. Consult Roberts<sup>16</sup> or Matthias et al.<sup>17</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.

bonding p-bands are separated by a low density of states band from the d-bands. The Fermi level for carbides or nitrides with 8 valence electrons, for example TiC, lies at the tops of the p-band, and for carbides or nitrides with 9 electrons, it lies at the bottom of the d-band (see Fig. 4). Piper,<sup>(21)</sup> on the basis of Hall coefficient measurements has modified this model so that the main band is filled as the valence electron concentration is increased from 8 to 10.

The importance of metal to nonmetal bonds in the carbides and nitrides is, however, not universally accepted. Dempsey,<sup>(22)</sup> for example, 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. 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. It is impossible on the basis of the present correlation, however, to distinguish between the Dempsey model and the Bilz model as both band structures result in a minimum in the density of states at a total valence concentration of eight and an increase in the density of states with the addition of more valence electrons. In order to interpret the critical temperatures of the carbides and nitrides, Toth et al.<sup>(15)</sup> assumed that the density of states is a minimum at 8 total valence electrons and reaches a maximum at about 10 total valence electrons.

To substantiate this 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 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.

## EXPERIMENTS AND DISCUSSION

### 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.<sup>(23, 13)</sup> and independently by Clougherty et al.,<sup>(24)</sup> it was reported that the cubic  $\alpha\text{-Mo}_3\text{C}_2$  crystallizes from the molten state at about 2600°C. At approximately 2200°C cubic  $\alpha\text{-Mo}_3\text{C}_2$  transforms very rapidly into the related hexagonal phase,  $\eta\text{-Mo}_3\text{C}_2$ . The composition of this hexagonal phase is not at MoC as originally believed. Because the transformation from the cubic to the hexagonal forms 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 work a series of samples in the Mo-C binary system were quenched from five different temperatures, 1650, 2200, 2320, 2415, and 2650°C into liquid tin or into oil. 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  $\eta\text{-Mo}_3\text{C}_2$ , the samples from 2200°C were mainly  $\eta\text{-Mo}_3\text{C}_2$  but had partially transformed to cubic  $\alpha\text{-Mo}_3\text{C}_2$ , while the samples quenched from higher temperatures were mainly cubic  $\alpha\text{-Mo}_3\text{C}_2$ .

The critical temperature of the cubic  $\alpha\text{-Mo}_3\text{C}_2$  quenched from 2415°C in Sn was 13.0°K with the transition extending from 13.5°K to 12.5°K. No 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  $\alpha\text{-Mo}_3\text{C}_2$  phase exists only over a small range of composition. The limited range of composition variation for the existence of this phase

Table II

## X-Ray Findings and Critical Temperatures in the Mo-C Binary System

Sample No.	Nominal composition Mo - C	Phase	Temperature of Quench °C	Critical temperature at middle of transition °K	Width of transition °K
1	60 - 40	$\eta\text{-Mo}_3\text{C}_2$ + trace $\text{Mo}_2\text{C}$	1650	9.0	0.4
2	58 - 42	$\eta\text{-Mo}_3\text{C}_2$	1650	9.0	0.2
3	60 - 40	$\eta\text{-Mo}_3\text{C}_2$ + $\alpha\text{-Mo}_3\text{C}_2$	2200	11.0	0.5
4	59 - 41	$\eta\text{-Mo}_3\text{C}_2$	2200	9.6	2.2
5	58 - 42	$\eta\text{-Mo}_3\text{C}_2$	2200	9.5	1.7
6	59 - 41	$\alpha\text{-Mo}_3\text{C}_2$ + trace $\eta\text{-Mo}_3\text{C}_2$	2320	12.0	1.2
7	56 - 44	$\alpha\text{-Mo}_3\text{C}_2$ + trace $\eta\text{-Mo}_3\text{C}_2$	2415	13.0	1.0
8	60 - 40	$\alpha\text{-Mo}_3\text{C}_2$ + $\eta\text{-Mo}_3\text{C}_2$	2650	12.2	2.9

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 critical temperature of the pure hexagonal  $\text{Mo}_3\text{C}_2$  quenched from  $1650^\circ\text{C}$  was  $9.0^\circ\text{K}$ . This temperature is nearly the same as the  $9.26^\circ\text{K}$  reported by Matthias and Hulm<sup>(4)</sup> for arc-melted specimens. The specimens quenched from  $2200^\circ\text{C}$  into tin had critical temperature varying from  $9.5$  to  $11.0^\circ\text{K}$ . 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  $1.28^\circ\text{K}$ . In a solid solution between  $\text{TaC}$  (NaCl) and  $\text{TaN}$ , it was found that the mean critical temperature of the cubic phase increased with increasing amounts of  $\text{TaN}$ . The width of the transition, however, also increased. The results show that the substitution of nitrogen for carbon in the  $\text{TaC}$  cubic phase increases  $T_c$  (Fig.5).

The experiments on  $\text{MoC}$  and  $\text{TaN}$  substantiate the proposed correlation of the superconducting properties of the carbides and nitrides. The critical temperature of  $\text{MoC}$  is the highest known transition temperature for any carbide and nearly equal to that of  $\text{NbN}$ . The substitution of nitrogen for carbon in  $\text{TaC}$  increased  $T_c$  as expected on the basis of the proposed band model. The present results and literature survey suggest that the

general features of the superconducting critical temperatures of the carbides and nitrides with the NaCl structure can be explained with the assumed band model.

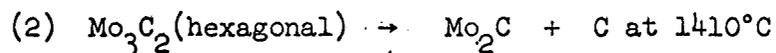
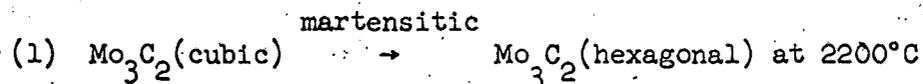
III. The Influence of Crystal Structure on the  $T_c$  of Hexagonal and Cubic Molybdenum Carbide.

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 the structural martensitic transformation that occurs in the phase change.

As Matthias and Hulm<sup>(4)</sup> pointed out, the hexagonal crystal structure is not as favorable for the occurrence of high  $T_c$ 's on these refractory compounds, as is the cubic structure. With the exception of technetium and MoN, elements and compounds crystallizing in a hexagonal structure seldom become superconducting above 5°K. The probable explanation of the high  $T_c$  for  $\eta$ -Mo<sub>3</sub>C<sub>2</sub> is that its crystal structure is very closely related to that of  $\alpha$ -Mo<sub>3</sub>C<sub>2</sub>. Nowotny et al.<sup>(26)</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 ~~one~~ 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 (see Fig. 6). Recent thermochemical data indicate that the transition from the  $\eta$ -Mo<sub>3</sub>C<sub>2</sub> to  $\alpha$ -Mo<sub>3</sub>C<sub>2</sub> is an order-disorder transition; the carbon atoms in  $\eta$ -Mo<sub>3</sub>C<sub>2</sub> appear to be ordered, while in  $\alpha$ -Mo<sub>3</sub>C<sub>2</sub> they occupy random

octahedral sites.

Because of the geometric similarities in the crystal structure between the hexagonal and cubic phase, the transformation is probably a martensitic one involving only a change in the sequential ordering of the atomic planes. A martensitic transformation would explain the need for the drastic quenches required to retain this phase. The transformations in the Mo-C binary system are as follows:



Reaction (1) which proceeds by a martensitic (i.e., diffusionless) reaction is the one we wish to suppress in order to retain the cubic phases. The classical martensitic microstructure by which this rapid transformation occurs is shown<sup>(23)</sup> in Fig. 7. In contrast to a nucleation and growth transformation, this martensitic transformation can occur simultaneously at all parts of the sample. 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 coherence length, the electronic changes would average over the structural changes. Indeed, if the compound is only partially transformed from the cubic to the hexagonal, the critical temperature is intermediate between that of the pure cubic and pure hexagonal. We believe that this is the first observation of a gradual change in  $T_c$  dependent upon the amount of martensitic transformation. If the compound is only

partially transformed from the cubic to the hexagonal, the critical temperature is intermediate between that of the pure cubic and pure hexagonal. This result suggests that there is a gradual electronic change which averages over the structural changes. The difference in the critical temperature of the two crystal modifications of MoC again indicates that both the electron concentration and the crystal structure are important factors in determining  $T_c$ .

#### IV. 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 Atomic International, Canoga Park, California. Preliminary results on MoC confirm the expectation that MoC is a high field type II superconductor.

#### CONCLUSION

Some of the important superconducting properties of the carbides and nitrides of the transition elements may be summarized as follows:

1. The critical temperatures of the carbides and nitrides increase with increasing amount of the nonmetal until stoichiometry is reached.
2. The superconducting transition temperatures of the carbides and nitrides are related to the total number of valence electrons. The critical temperature is a minimum when the total number of valence electrons is 8 and the critical temperature increases as this total increases.

3. The relationship between the maximum in critical temperature and the total number of electrons has not been fully established. The highest critical temperature for any carbide or nitride occurs at 17.8°K in the NbN-NbC pseudo binary system or at approximately 9.8 total electrons.

Acknowledgements

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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. (10)).
- Fig. 2. The variations in  $T_c$  with composition in the pseudo-binary NbC-TaC (after Wells et al. (11)).
- Fig. 3. Matthias's suggested explanation for the maximum in  $T_c$  in the NbC-TaC pseudo-binary system. The dotted lines refers to a hypothetical variation in  $T_c$  (after Matthias (12)).
- Fig. 4. The variation in the density of states with energy according to Bilz for the carbides and nitrides with the NaCl structure. Here  $\Sigma$  refers to the sum of the valence electrons of the metal and non-metal atoms.
- Fig. 5. The variation in  $T_c$  with composition in the TaC-TaN pseudo-binary system.
- Fig. 6. The crystal structure of hexagonal  $Mo_3C_2$  and cubic  $Mo_3C_2$  showing the sequential ordering of the atomic planes. In hexagonal  $Mo_3C_2$  the positions of the carbon atoms are not known. The figure shows only the possible location of the carbon atoms and corresponds to the formula MoC, not  $Mo_3C_2$ .
- Fig. 7. A typical martensitic type microstructure resulting from the diffusionless transformation of cubic to hexagonal  $Mo_3C_2$  after Rudy et al. (23). The surface upheavals on the prior electrostatically polished surface are revealed by contrast interference microscopy.

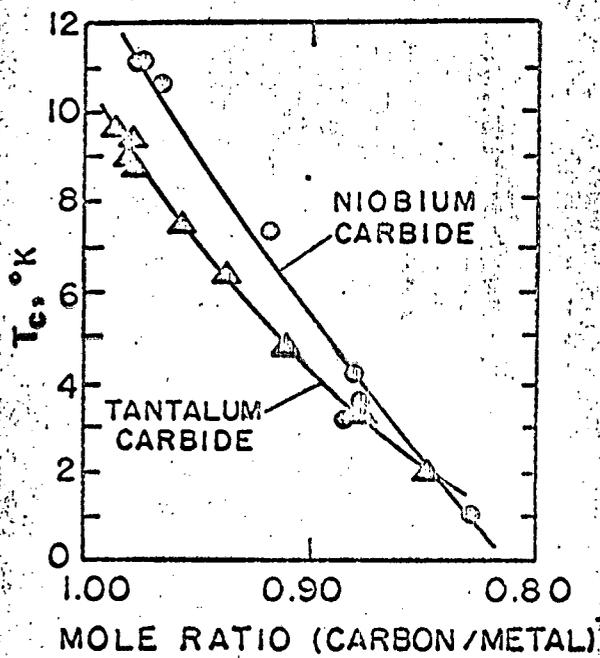


Fig. 1

FIG. 1

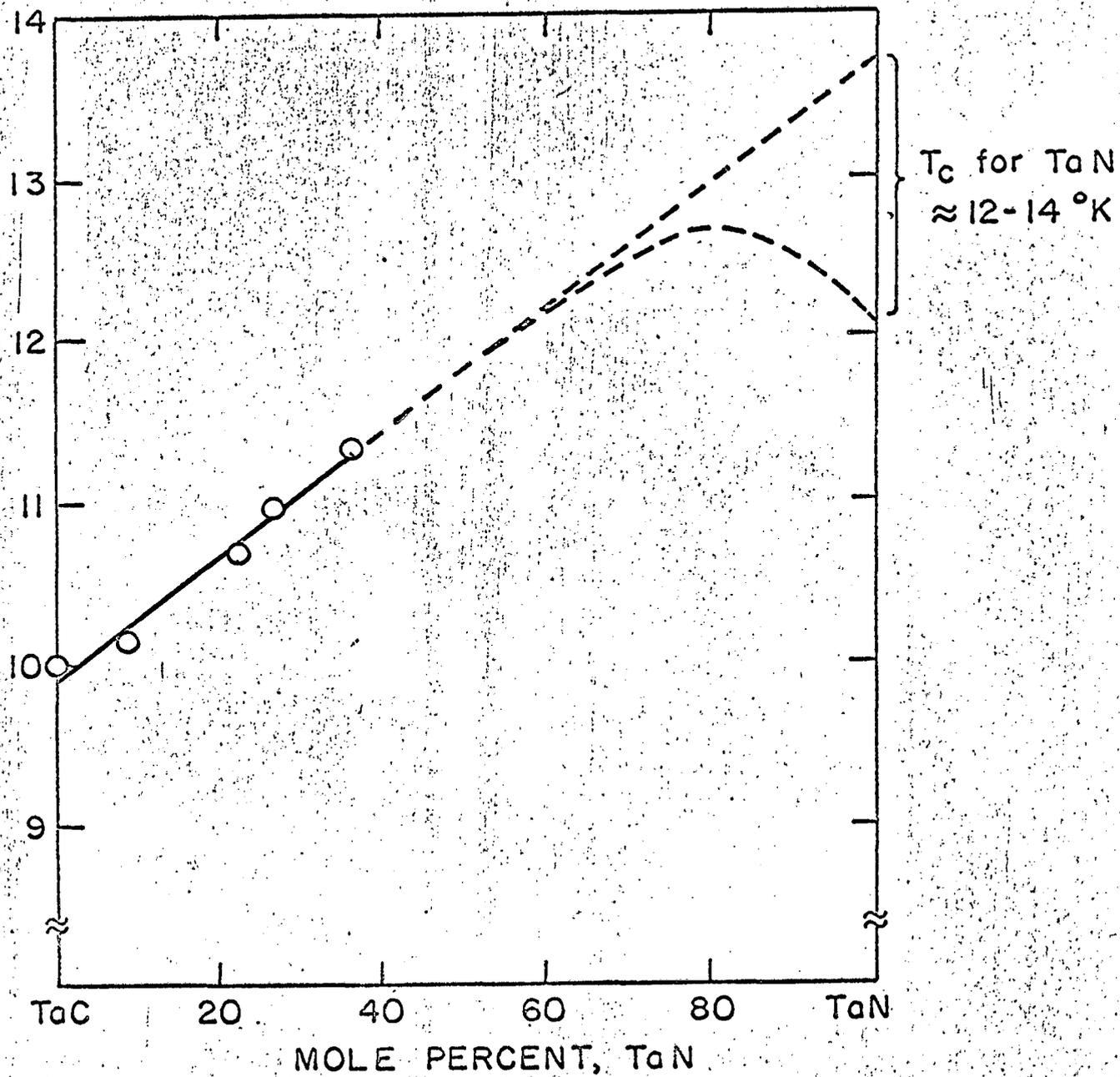
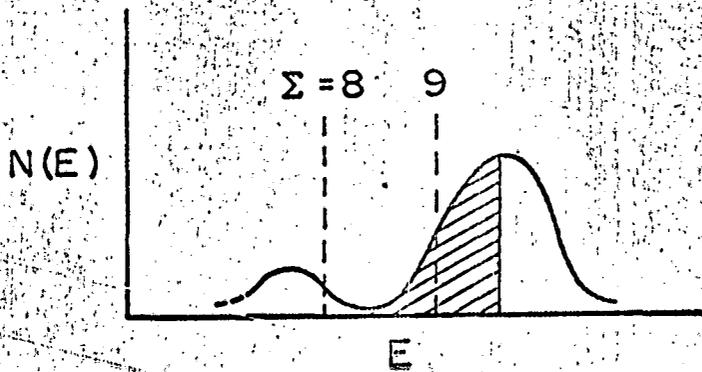
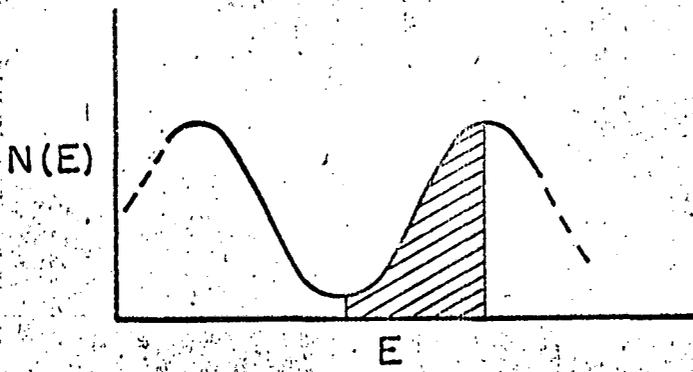


Fig. 2

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(a)



(b)

Fig. 3

Fig 3

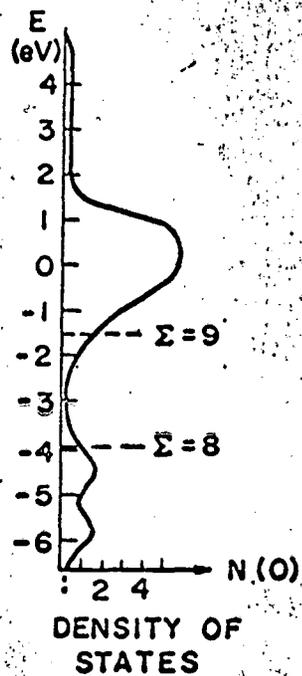


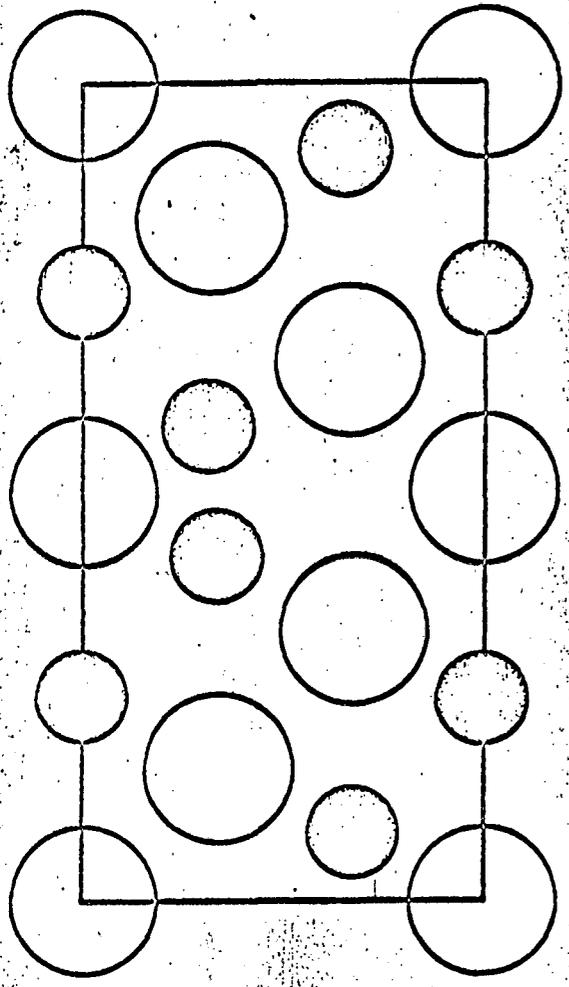
Fig. 4

Fig. 4



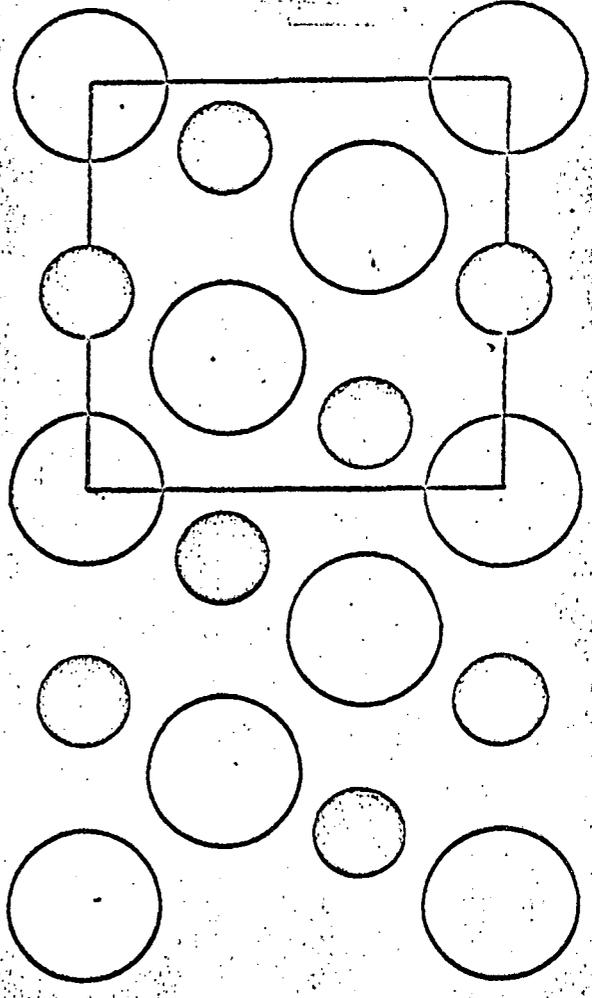
Fig: 5 (None available)

$\eta$  Mo<sub>3</sub>C<sub>2</sub>



ABCACB, ABCACB

$\alpha$  Mo<sub>3</sub>C<sub>2</sub>



ABC, ABC

Fig. 6

Fig. # 6



Fig. 7

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