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SUPERCONDUCTIVITY OF THE CUBIC MODIFICATION OF MoC

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Louis E. Toth,* Erwin Rudy,** Jean Johnston,+ and Earl R. Parker+

Abstract

The superconducting transition temperatures of the metallic carbides and nitrides with the NaCℓ structure are interpreted on the basis of the tight-binding model of Bilz.[1] It is found that total valence electron concentrations from 9 to 10 are required for high critical temperatures in these compounds. The cubic modification (NaCℓ) of molybdenum carbide has been found to be superconducting at 13.0°K in agreement with the Bilz band model.

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INTRODUCTION

Accumulating evidence indicates that the electron-to-atom (e/a) ratios of approximately 5 or 7,[2,3] generally considered to be necessary for high critical temperature superconductivity, need not always be satisfied. Data reported herein indicate that the critical temperatures of carbides and nitrides may be markedly influenced by the crystal structure as well as by the electron-to-atom ratio. This idea is clearly demonstrated in the investigation of the critical temperature of the two crystal modifications of molybdenum carbide.

The observed critical temperatures of the nitrides and carbides with the NaCℓ structure (B1) may be understood with the aid of the tight-binding calculations of Bilz.[1] According to this model, the hardness, brittleness, and high melting temperatures of these compounds indicate the formation of strong bonds between the nonmetal p-wave functions and the sp^3d^2 hybrid functions of the transition metal. The importance of these strong nonmetal-to-metal bonds had been originally formulated by Rundle[4] and Krebs.[5] On the basis of a tight-binding calculation, Bilz has found that the bonding p-bands are separated by a low density of states band from the d bands. The Fermi level for TiC, with eight valence electrons, lies at the top of the p-band, and TiN, with 9 electrons, lies at the bottom of the d-band (see Fig. 1). In this model a minimum in the density of states occurs at approximately 8.5 electrons. Piper,[6] 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.

In the present paper, we shall assume that the density of states is a minimum at the total electron concentration of 8 (per formula) and reaches a maximum when the total electron concentration is between 9 and 10. With this band structure, the variation of most of the critical temperatures of the transition

metal carbides and nitrides with the NaCℓ structure can be understood. The critical temperatures of the carbides and nitrides with 8, 9, and 10 total valence electrons are shown in Table I. The table is arranged to place the nitrides of the IIIa group metals next to the carbides of the IVa 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 $VC_{0.88}$ contains only 8.5 total electrons. The highest T_c is for NbN with 10 total valence electrons. The compound VN, also containing 10 valence electrons, has a lower transition temperature, but this may be due to individual departures from the general band scheme as Piper's Hall coefficient measurements of VN indicate.[6] In general, the carbides and nitrides with the same number of valence electrons have nearly the same critical temperatures. This correlation does not seem to apply to the nitrides and carbides of uranium and thorium.

The critical temperature depends not only on the total number of electrons but also on the crystal structure. For example, TaN, with 10 electrons, is normal down to 1.20°K but its crystal structure is hexagonal.

Inspection of this table further suggests that the three carbides, CrC, MoC, and WC, with the NaCℓ structure may have high critical temperatures because they have 10 total electrons. A cubic modification of CrC definitely does not exist,[7] but high temperature cubic modifications have been found for MoC and WC. Of these latter two compounds, only MoC can be stabilized in the cubic form at ambient temperatures. Niobium and molybdenum exist in the same row, and so the

Table I

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

Group IIIa nitrides			Group IVa 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 IVa nitrides			**Group Va 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 Va nitrides			**Group VIa carbides**		
VN	10	8.2°K	CrC	10	Does not exist with NaCℓ structure.
NbN	10	15.8°K	MoC	10	Present investigation
TaN	10	Does not exist with NaCℓ structure.	WC	10	Exists at high temperatures only.

* Values quoted are those listed by Roberts[8] and Matthias et al.[9]

** "Normal" means not superconducting at about 1°K. Consult Roberts[8] or Matthias et al[9] for the exact temperatures.

*** $VC_{0.88}$ is the highest carbon ratio which can be obtained by usual techniques; this composition corresponds to 8.5 electrons.

critical temperature of MoC should be very nearly the same as that of NbN (15.6°K). However, Matthias et al.[10] have suggested that the cubic form of MoC should be superconducting at about 10.6°K. Their prediction was based on test results from a series of solid solutions between refractory compounds with the NaCℓ structure and the hexagonal MoC.

The Cubic Form of MoC

A high temperature phase at the composition MoC, with a hexagonal unit cell, has been known to exist for some time.[11] Only recently has the cubic modification been found. In an investigation of the Mo-B-C ternary system, two of the present authors (E.R. and L.T.)[12] found in arc-melted samples a new phase with an NaCℓ (B1) crystal structure at the approximate composition $Mo_3C_{1.9}B_{0.1}$. After a careful examination of this area of the ternary diagram, it was also discovered that the hexagonal form of molybdenum carbide formed at the composition Mo_3C_2 and not at MoC. Independently, Clougherty et al.[13] synthesized the cubic modification of MoC by the application of high pressures and temperatures. They confirmed the Mo_3C_2 composition for the hexagonal phase and also found that the cubic modification existed at the composition MoC_{1-x} (reported as $MoC_{0.72+x}$ by Clougherty[13]). One of the present authors (E.R.)[14] obtained the cubic modification by rapidly quenching samples from 2800°C onto a water-cooled copper plate.

On the basis of these experiments, it was established that the cubic modification α-MoC_{1-x} crystallizes from the molten state at about 2600°C. At approximately 2200°C, α-MoC_{1-x} transforms very rapidly into the related hexagonal η-Mo_3C_2 (see Fig. 2). Below 1450°C, η-Mo_3C_2 decomposes slowly into Mo_2C (which has orthorhombic crystal structure) and free carbon. It was further established that the α-form could be stabilized by small amounts of boron, uranium, or thorium.[14]

The crystal structure of the hexagonal Mo_3C_2 is very closely related to that of the cubic modification. Nowotny et al.[11] have found that this phase has a hexagonal unit cell belonging 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 as a subcell the B1 sequential ordering ABC, ABC. (See Fig. 2.) Recent thermochemical data indicate that the transition from the η-Mo_3C_2 to α-MoC_{1-x} is an order-disorder transition;[7] the carbon atoms in η-Mo_3C_2 appear to be ordered, while in α-MoC_{1-x} they occupy random octrahedral sites.

In the present investigation, these experiments on molybdenum carbide were repeated to determine the superconducting critical temperature of both the α and η forms.

EXPERIMENTAL

The materials for this investigation consisted of 99.9+% molybdenum powder (< 74 microns; impurities: W 200 ppm, C 24 ppm, O_2 24 ppm, and Si 100 ppm), amorphous boron powder (96% B, the rest mainly B_2O_3) and lampblack. Well-mixed powders placed in a graphite die were hot pressed at temperatures that would just start the melting reaction. Since Mo_3C_2 is stable in the presence of graphite, there was no reaction with the graphite die.

Series of samples in the Mo-C binary system were quenched from five different temperatures: 1650, 2200, 2320, 2415, and 2650°C. The samples from the 1650, 2200, 2320, and 2415°C treatments were quenched in liquid tin, and the samples from 2650°C in oil. In order to quench the samples in tin, the hot-pressed samples were placed in a graphite die, the bottom end of which was shortened so that the die could be broken with the application of pressure. A graphite plunger sealed off the top end of the die and transmitted pressure. The samples were first held at the chosen temperatures for 10 minutes. This period

was adequate for the formation of the hexagonal phase as well as for the cubic phase, which forms very rapidly. Pressure was then applied, the bottom of the die broke off, and the sample dropped into a molten tin bath. To quench the material from the molten state, samples were placed in a graphite die having a 1 mm diameter hole in the end of the die, the samples were heated to 2650°C (which is above their melting temperature), and pressure was then applied to the plunger to force the molten samples out the small hole and into the oil. The outer surfaces of the quenched samples were ground off to remove any phases that might have been formed by reactions with tin or oxygen. The samples quenched in tin 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 quenched samples were also examined with metallography techniques.[12]

EXPERIMENTAL RESULTS

The results of the x-ray analysis are listed in Table II. The samples quenched from 1650°C showed only the hexagonal η-Mo_3C_2, the samples from 2200°C were mainly η-Mo_3C_2 but had partially transformed into α-MoC_{1-x}, while the samples quenched from 2320, 2415 and 2650°C were mainly α-MoC_{1-x}. The transformation from the cubic phase to the hexagonal phase involves only a shift in the sequential ordering (see Fig. 2); hence, this transformation proceeds at an extremely rapid rate. An intensity comparison of the (012) and (104) lines in the x-ray pattern of the hexagonal phase (the same as the (111) and (200) lines in the cubic phase) showed that the samples quenched from 2200°C were partially transformed from the cubic phase into the hexagonal phase. The samples quenched at 2320, 2415 and 2650°C were mainly cubic but some of the hexagonal phase was present. (See Fig. 3)

The critical temperature of the α-MoC_{1-x} quenched from 2415°C in Sn was 13.0°K with the transition extending from 13.5°K to 12.5°K (see Table II). No variation could be detected in T_c with either a change in composition or with the slight addition of boron. The relative insensitivity of T_c to changes in composition is due to the small range of composition over which α-MoC_{1-x} exists. The limited range of composition is related to its limited stability.[7] The samples quenched from 2650°C in oil had broad transitions partly due to the small particle size of the specimen which resulted from brittle shattering upon quenching and partly due to the partial transformation to the hexagonal phase, which could not be completely arrested.

The critical temperature of the pure hexagonal η-Mo_3C_2 quenched from 1650°C was 9.0°K with the width of the transition being about 0.4°K. This temperature is nearly the same as the 9.26°K reported by Matthias and Hulm[15] for arc-melted specimens. The specimens quenched from 2200°C into tin had critical temperatures 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 of the sample with the transition temperature of 11.0°K showed that it contained the most amount of the B1 phase of any of the samples quenched from 2200°C

DISCUSSION

The observed critical temperature of 13.0°K for α-MoC_{1-x} is the highest known critical temperature for any binary carbide and is one of the highest critical temperatures for any binary phase. This value is exceeded by only six binary β-tungsten phases[16] and by 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.

Table II.

X-Ray Findings and Critical Temperatures in the Mo-B-C Ternary System

Sample No.	Nominal composition Mo - B - C	Phase	Heat Treatment	Critical temperature at middle of transition	Width of transition
1	60 - 0 - 40	η-Mo_3C_2 + trace Mo_2C	H.P. + 1650°C Sn	9.0°K	0.4°K
2	58 - 0 - 42	η-Mo_3C_2	H.P. + 1650°C Sn	9.0°K	0.2°K
3	60 - 0 - 40	η-Mo_3C_2 + α-MoC_{1-x}	H.P. + 2200°C Sn	11.0°K	0.5°K
4	59 - 0 - 41	η-Mo_3C_2	H.P. + 2200°C Sn	9.6°K	2.2°K
5	58 - 0 - 42	η-Mo_3C_2	H.P. + 2200°C Sn	9.5°K	1.7°K
6	59 - 0 - 41	α-MoC_{1-x} + trace η-Mo_3C_2	H.P. + 2320°C Sn	12.0°K	1.2°K
7	56 - 0 - 44	α-MoC_{1-x} + trace η-Mo_3C_2	H.P. + 2415°C Sn	13.0°K	1.0°K
8	60 - 0 - 40	α-MoC_{1-x} + η-Mo_3C_2	H.P. + 2650°C oil	12.2°K	2.9°K
9	47 - 3 - 51	α-MoC_{1-x} + η-Mo_3C_2	H.P. + 2650°C oil	12.5°K	3.0°K

The critical temperature for α-MoC_{1-x} is nearly the same as the critical temperature of NbN. The present results and survey of the literature (Table I) suggest that the general features of the superconducting critical temperatures of the carbides and nitrides with the B1 structure can be explained with aid of the band models proposed by Bilz[1] and Piper.[6] The density of states is a minimum at a total valence electron concentration of about 8 (or 8.5) and increases to a maximum at about 10 (or slightly less). Although the general superconducting features can be explained with this band model, the details of the band structure appear to vary from element to element. For example, the critical temperatures of B1 solid solutions between NbC and TaC have been found to go through a maximum;[17] this result cannot be explained with this simple model.

It is important to emphasize that the electron concentrations needed for high T_c's in these compounds also depend upon the crystal structure. These requirements for total number of electrons are not the same as the electron-to-atom ratios postulated by Matthias for the transition metals where the density of states does not seem to vary significantly with changes in crystal structure.[18]

The influence of crystal structure is clearly seen for TaN, with 10 electrons, which is not superconducting, probably because of its hexagonal crystal structure. Its influence is further demonstrated by examining the crystal structure of η-Mo_3C_2, which has a relatively high critical temperature for a hexagonal crystal. With the exception of technetium and MoN, elements and compounds crystallizing in a hexagonal structure seldom become superconducting above 5°K. The probable explanation for the unusually high T_c for η-Mo_3C_2 is that its crystal structure is very closely related to that of α-MoC_{1-x}. The unit cell is just two NaCℓ unit cells placed on top of one another in an inverted order (Fig. 2). 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.

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Figure Captions

Figure 1 - The variation in the density of states with energy according in Bilz[1] for the carbides and nitrides with the NaCℓ structure. Here Σ refers to the sum of the valence electrons of the metal and nonmetal atoms.

Figure 2 - The crystal structure of η-Mo_3C_2 and α-MoC_{1-x} showing the sequential ordering of the atomic planes. In η-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.

Figure 3 - Diffractometer results showing the transformation in crystal structure from η-Mo_3C_2 (sample 3) to α-MoC_{1-x} (samples 6 and 7). The diffractometer results of samples six and seven are very nearly alike even though one sample has a higher transition temperature than the other.

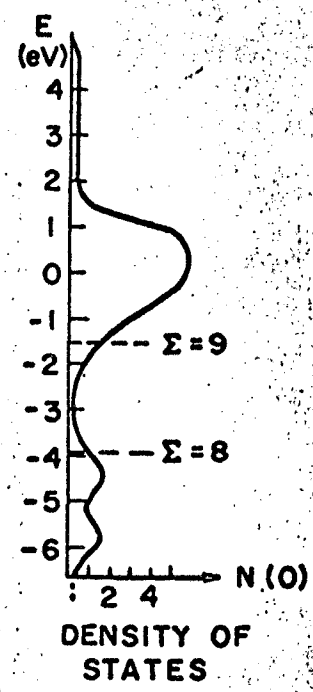

Fig. 1.

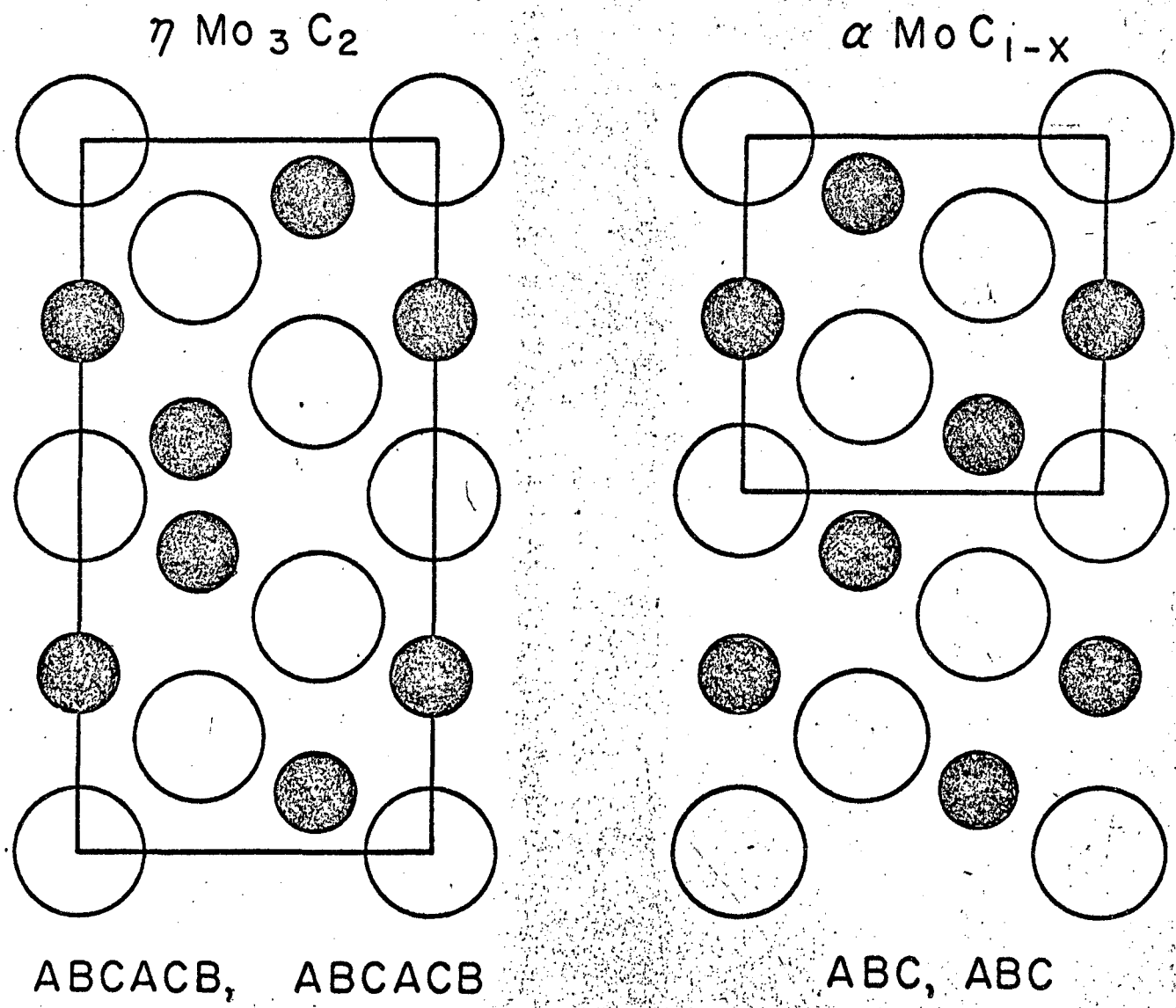

Fig. 2.

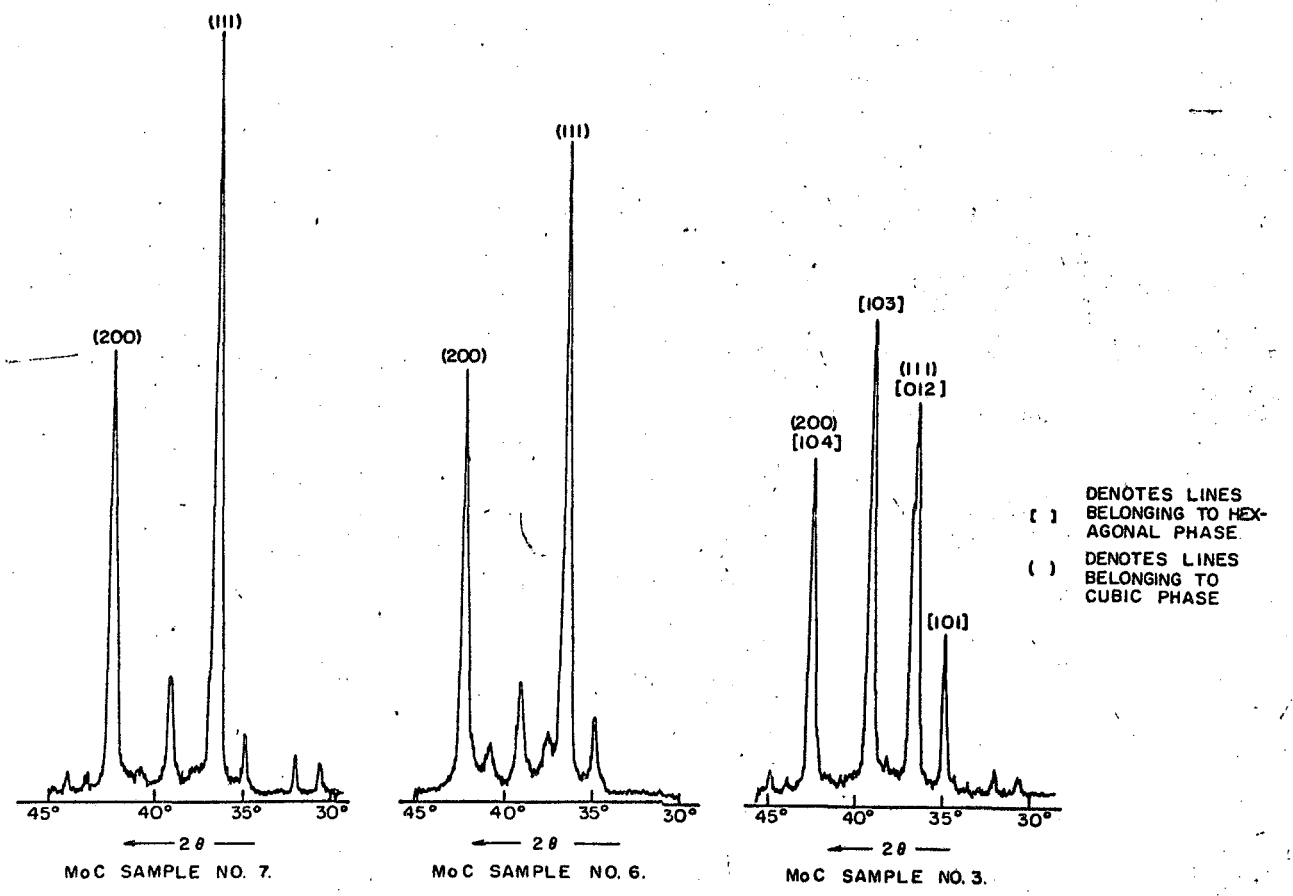
(111)
(200)
45°
40°
35°
30°
2θ
MoC SAMPLE NO. 7.
(111)
(200)
45°
40°
35°
30°
2θ
MoC SAMPLE NO. 6.
[103]
(111)
[012]
(200)
[104]
[101]
45°
40°
35°
30°
2θ
MoC SAMPLE NO. 3.
[ ] DENOTES LINES BELONGING TO HEXAGONAL PHASE
( ) DENOTES LINES BELONGING TO CUBIC PHASE
MUB-4370

Fig. 3.

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