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SUPERCONDUCTIVITY OF CERAMIC COMPOUNDS

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Chapter in Ceramic Microstructures

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INTRODUCTION

The existence of superconductive ceramic compounds has been recognized for more than thirty-five years. In the early 1930's the interest level in superconductivity was high. This active period was followed by one of decline until 1961 when there was a rekindling of interest because of the discovery of high-magnetic-field high-current-density superconductors. In the years between 1930 and 1955, some research was done on ceramic superconductors because a few of them were known to have high critical temperatures. Characterization of their properties was hampered, however, because of the difficulties involved in preparing specimens and the problems encountered in identifying the important microstructural features.

Ceramic superconductors comprise a large class, ranging from transition metal borides, carbides, nitrides and oxides (including $SrTiO_3$, one of the most recently discovered compounds). Some of these materials are of potential practical importance because of their high-field properties, whereas others are of interest only because they help to provide an understanding of superconductive behavior which may lead to a better fundamental understanding of the solid state. The materials aspect of superconductivity is particularly intriguing because of the sensitivity of certain parameters, particularly the critical current, to microstructure.

A simple comparison of the electrical power necessary to operate conventional and superconducting solenoids illustrates one reason that high-field superconductivity is receiving so much attention. Specially designed conventional solenoids, such as those in the National Magnet Laboratory, can generate steady magnetic fields up to 90kG in a two-inch bore for extended periods of time. However, to produce a 90kG field, a current of 10,000A at about 250v (i.e., about 2.5MW of electrical power) is required. Once a steady field is established, the electrical power merely generates heat which requires about 1000 gallons per minute of de-ionized water for removal. A superconducting solenoid could generate an identical field in the same volume with only ten amperes (available from a power supply such as an automobile battery) or about 120 watts. The total electrical power expenditure in a superconducting magnet is negligible in comparison to that consumed by a conventional solenoid, and it is from this that the technological significance stems. Cooling a superconducting solenoid to very low temperatures necessitates the use of liquid helium and cryogenic liquid containers, but even with this handicap, the total cost of operating a small-bore superconducting solenoid is only a small fraction of that for a conventional solenoid.

SUPERCONDUCTIVITY

A brief introduction to the phenomenology of superconductivity will be presented herein. For more comprehensive accounts the reader is referred elsewhere.[1-3]

The most striking property of superconductors, which led to the discovery of superconductivity in 1911 by H. Kamerlingh Onnes, is the lack of electrical resistivity below a critical temperature, T_c, which separates superconductive and normal states. The temperature variation of resistivity

(Fig. 1) shows this characteristic behavior for a solid-solution alloy (75Nb-25Zr) and for a ceramic superconductor. The resistivity of a superconductor is truly zero according to experiment as well as theory. Unlike superconductors, materials such as copper with high normal conductivity show a continuous decrease in resistivity down to the lowest testing temperatures attainable. At room temperature, good normal conductors have lower resistivities than many superconductors. At low temperatures, although the resistivity of the normal metals may be very small, it is still many orders of magnitude larger than the resistivity of superconductors.

The highest known critical temperature is about 18.1°K (for Nb_3Sn), as is shown in Table I (Refs. 4 and 5); not much lower (17.8°K) is that for 70 mole % NbN-30 mole % NbC.

A second unique property of superconductors is that they are perfectly diamagnetic at low magnetic fields, i.e., magnetic flux is completely excluded from the bulk of the superconductor. This is illustrated by the magnetization curve for an ideal superconductor* shown in Fig. 2. It is an experimental fact that $-4\pi M = H$ (or $B = 0$) at low fields. One class of superconductor (Type I) remains perfectly diamagnetic up to a critical field, H_c, where a first-order phase transition to normal behavior occurs; bulk Type I materials are low-field superconductors, i.e., H_c does not exceed a few thousand gauss. The other class of superconductor (Type II) is perfectly diamagnetic only up to the "lower critical field" H_{c_1}, where

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* Long, cylindrical specimens whose axes are parallel to the applied magnetic field are used in order to avoid demagnetization effects.

magnetic flux begins to penetrate the specimen; such samples, however, remain largely superconducting up to an "upper critical field" H_{c_2}, above which normal behavior occurs. Between H_{c_1} and H_{c_2}, a superconductor is said to be in the "mixed state", a condition in which normal filaments containing magnetic flux ("fluxoids") are surrounded by a superconducting matrix. The Type II class of superconductors includes all high-field superconductors; H_{c2} may be 100 times larger than H_c.

The upper critical field is temperature dependent (Fig. 3), rising from zero at T_c to a maximum value at absolute zero. This curve separates the superconducting region from the normal area. High-field properties can only be obtained at temperatures well below T_c. Consequently, the higher the value of T_c, the easier it is to make use of high-field superconductivity at liquid helium temperature (4.2°K).

A third important superconductive property is the critical current density J_c. Critical current density is conventionally taken to be the current density (at $T < T_c$ and $H < H_{c_2}$) which causes the onset of resistive behavior. It is a function of temperature and of magnetic field. For an ideal Type II material with a reversible magnetization curve, J_c should be extremely small. There is a Lorentz force interaction between the current and the fluxoids which leads to fluxoid motion and thus to resistive behavior. However, if the fluxoids are "pinned" so that they cannot move, J_c can become very large (and a hysteresis develops in the magnetization behavior). Fluctuations in chemical composition on a microstructural scale can lead to fluxoid pinning, and J_c has been found to be microstructure-sensitive, as shown in Fig. 4 for an Nb-Zr alloy.

Plots of critical current density vs applied transverse magnetic field (at constant temperature) show the superconductive and resistive

behavior conditions. Such curves are shown in Fig. 5 for the same material in two different microstructural states. The zero current density intercept gives H_{c_2}. Also indicated on the figure are two possible "operating states" for superconducting solenoids designed to generate a maximum magnetic field of 0.7 H_{c_2} (about 49 kG in this case). The operating conditions for such solenoids are restricted to the superconductive region where $\rho = 0$. The ends of the "design reference" curves were kept somewhat below the respective J_c vs H curves to provide a safety factor. The importance of a large critical current density for solenoid applications is evident from an examination of the simple solenoid equation:

$$H = 0.4\,\pi n I$$

which can be written in the more useful form

$$H = 0.4\,\pi\lambda\, Jt,$$

where H is the field generated by the solenoid (in gauss), n is the number of turns per cm, I is the current (in amperes), λ is the geometrical packing factor of the superconductive windings (i.e., the fraction of the solenoid winding cross section occupied by the superconducting wire), J is the current density (in A/cm^2), and t is the thickness of the solenoid windings (in cm.). Since J is limited by the material property J_c, it is apparent that a solenoid made of the material with the lower J_c (Fig. 4) would require thicker windings than one made of the material with the higher J_c. At the "operating state" ($J = 1.5 \times 10^4$ A/cm^2) selected to produce a field of 49 kG with the material of low J_c it is necessary that $t \approx 6.5$ cm, if a reasonable packing factor ($\lambda = 0.4$) is chosen. At the "operating state" ($J = 7.5 \times 10^4$ A/cm^2) for the material of high J_c a thickness of only 1.3 cm is required.

High J_c values are important economically, but another factor also imposes a limit on the current that can pass through a superconducting solenoid. A hoop-stress is generated in the solenoid windings because of the magnetic field generated by the current passing through the wire. For a solenoid that will provide a certain field, the higher the current density, the higher will be the hoop-stress. This stress must not be allowed to exceed the yield stress for a ductile material or the fracture stress for a brittle material.

EMPIRICAL GUIDES

Although there have been great theoretical advances in the last ten years, it is not yet possible from theory alone to predict either the occurrence of superconductivity or the magnitude of the superconductive properties. Thus, it is necessary to rely upon empirical guides, the most important of which were first proposed by B. T. Matthias.[7,8] These are, briefly, (1) certain crystal structures are favorable for the occurrence of superconductivity, and (2) critical temperature is a systematic function of the number of valence electrons per atom.

Superconductivity occurs at the highest temperatures for materials having crystal structures with high symmetry, such as cubic. Little has been said about the local arrangements of atoms in a crystal, although this feature is known to be important, but more extensive studies are necessary to clarify this point.

The qualitative variation of T_c with the number of valence electrons per atom (e/a), as shown in Fig. 6, has been well substantiated for elements, metallic solid-solutions, and, to some extent, intermetallic compounds. The transition metal series comprise a particularly interesting region where, in the absence of ferromagnetic or antiferromagnetic

behavior, maximum values of T_c occur at e/a ratios somewhat below 5 and somewhat below 7. The use of e/a ratios for predicting composition of ceramic compounds (such as the carbides) having high critical temperatures requires that all atoms must be included. On such a basis the maximum in T_c occurs at the commonly observed e/a ratio of approximately 5. However, on the basis of the total number of valence electrons per transition metal atom (e/t), T_c is a maximum for e/t = 10; see Table II.[9]

We would expect MoC and WC, which exist with the NaCl structures only at high temperatures, to have high critical temperatures. These compounds can be retained in the NaCl structure by means of rapid quenching. As shown in Table III, the anticipated high values of T_c were obtained with quenched specimens. Furthermore, a comparison of T_c for equilibrium and metastable structures indicates that the NaCl structure is more favorable than the hexagonal structure.

The T_c data in Tables II and III are presented as if each compound existed only at a fixed stoichiometry. Actually, all of the compounds have ranges of composition, and it is not unlikely that T_c will vary with composition. The literature contains scattered T_c data for ceramic compounds. Giorgi and co-workers[12] measured the T_c of niobium carbide and tantalum carbide in the NaCl structure as a function of composition. They showed how variable the experimental results can be (Fig. 7). A change of carbon content of less than 6 atomic percent in NbC_{1-x} changed T_c from below 1°K to over 11°K. Since the critical temperature can be extremely sensitive to composition change, it follows that the effects of impurities on T_c may also be large.

The three primary factors that affect the critical temperature of superconducting ceramic compounds are crystal structure, deviations from

the composition, and impurity content. Good control and knowledge of these factors are necessary in superconductivity investigations.

The theory of superconductivity for high-field Type II materials is reasonably well developed. In principle, one can predict the upper critical field at a given temperature with fair accuracy from a knowledge of T_c, the normal-state (residual) resistivity, and the normal-state electronic specific heat coefficient. The critical temperature can be measured readily, but the specific heat coefficient is somewhat difficult to determine. Therefore, it is usually easier to determine experimentally H_{c_2}. There are no reliable empirical guides for estimating the variation of H_{c_2} with composition, microstructure or crystal structure. The existance of high critical temperature is no assurance that H_{c_2} will also be high.

CERAMIC SUPERCONDUCTORS

Early investigators studying the superconductivity of ceramic compounds generally were not concerned with minor composition variations. Some early determinations of critical temperatures were surprisingly accurate compared to results reported later (e.g., work by Meissner and co-workers[13-17] and by McLennan et al.[18]). One especially interesting result was that of Meissner, Franz and Westerhoff[17] who, in 1933, found an indication of superconductivity for NbO. Although these early workers questioned the reliability of this result, the superconductivity of NbO was confirmed in 1964.[19] In the 1940's and early 1950's, superconductive niobium nitride attracted attention because of its high critical temperature (over 14°K).[20-25] The extensive investigation of NbN by Rögener[24] in 1952 has remained the most significant work until recently.

During the past decade Matthias, Hulm and co-workers[26-32] have discovered many new superconducting compounds. In their work, they used a magnetic testing technique, rather than the commonly-used resistive technique, to determine T_c in order to eliminate the possibility of a bulk specimen appearing to be superconductive whereas the results might be due to small, continuous filaments of a second phase. In retrospect, it seems likely that a magnetic technique might also yield misleading results when a thin continuous superconducting grain boundary phase was present. Until the work of Giorgi et al.[12] on NbC and TaC, however, the effects of stoichiometry variations and impurities were virtually ignored.

A. Current Research

Recent investigations have been mainly involved with studies of ceramic compounds having the NaCl (B1) structure. Williams et al.[33] prepared cubic NbN compounds in a previously unexplored composition range. The critical temperatures of these low-oxygen materials were found to be higher than has been reported, and the variation of T_c with composition was found to be such that the maximum T_c (17.3°K) occurred somewhat below the ideal stoichiometric composition (Fig. 8). This maximum value is rather close to that predicted by Geballe et al.[36] for high-stoichiometry NbN. Pessall et al.[35,37] and Williams et al.[38] have also investigated the variation of critical temperature with composition for cubic niobium carbo-nitrides near stoichiometry (Fig. 9). The NbN-rich solid solutions of Pessall et al. were evidently somewhat below stoichiometry, as is indicated by the low reported T_c values, and the NbC-rich solid solution may have been slightly below stoichiometry, as is indicated by the low T_c value for "pure" NbC (less than the 12.0°K

for $NbC_{1.0}$).[39]

When various T_c data for NaCl structure ceramic compounds and their solid solutions (based on transition elements of the second and third long periods), as well as for fcc alloys based on iridium, are plotted as a function of valence electrons per atomic volume of the pure metallic elements involved, a single curve results (Fig. 10). This suggests a uniform electronic band structure, or, more correctly, a uniformly varying band structure for these materials. One implication from these data is that critical temperatures higher than 17.8°K are not likely to be found for NaCl structure ceramic compounds.

At the Westinghouse Research Laboratories, extensive investigations of NaCl structure compound solid solutions are in progress.[35,37,40] All of the solid solutions investigated have been variations of either NbN or a high T_c niobium carbo-nitride. Pessall and co-workers[35,40] have measured the upper critical fields of these solid solutions and the critical current densities as a function of applied transverse magnetic field.

For niobium carbo-nitrides near stoichiometry, the H_{c_2} values at 4.2°K of Pessall et al.[35,40] and of Williams et al.[38] are shown in Fig. 11. Although the former found a peak in H_{c_2} between 10 and 20 mole % NbC in NbN, these results of Pessall et al. can be explained if it assumed that their niobium nitride had a sub-stoichiometric composition. Williams et al. found H_{c_2} to decrease continuously (solid line in Fig. 11) with increasing NbC content. This behavior, with H_{c_2} varying from about 118 kG for NbN near stoichiometry to about 12 kG for NbC, contrasts sharply with the critical temperature behavior (Fig. 9) where T_c varies from 17.3°K for NbN and 17.8°K for $NbC_{0.3}N_{0.7}$ to about

10-12°K for NbC. While T_c decreases only about 40%, H_{c_2} decreases almost 90%; thus, a high T_c does not necessarily indicate the existence of a high H_{c_2}, and so separate measurements of T_c and H_{c_2} are necessary to characterize superconductors. The highest upper critical fields found to date for NaCl structure ceramic compounds at 4.2°K are about 133 kG for an NbN-TiN solid solution[35] and about 132 kG for NbN containing a small amount of oxygen.[38]

The variation of the critical current density (J_c) as a function of the applied transverse magnetic field has received cursory attention only.[35,41-43] Some results indicate that J_c is exceptionally low ($\sim 10^2$ A/cm^2) for NaCl-type compounds,[41] however, no one has varied the microstructure systematically and studied the resulting J_c levels. Certainly the possibility of obtaining high J_c levels exists, as is indicated by the literature on metallic solid solutions and by the preparation of fine NbC-NbN whiskers[42] with $J \sim 10^5$ A/cm^2. Tests in longitudinal magnetic fields result in high current density measurements,[43] but these are of little practical importance because the transverse-field J_c is the limiting factor in solenoid applications. Furthermore, whereas H_{c_2} values in the range 120-130 kG at 4.2°K are potentially useful, niobium-titanium metallic solid solutions have only slightly lower H_{c_2} values and are much easier to fabricate. Results to date indicate that future work should be directed toward the discovery of new ceramic compounds with higher upper critical fields, and crystal structures other than the NaCl type should be investigated.

B. Future Work

Complex carbides and nitrides having the β-Mn (A13) structure appear to be especially favorable for superconductivity. The first superconductor with this structure, Mo_3Al_2C, was discovered in 1964,[44] and only three have been found to date (see Table IV). Why this structure is promising can be seen through a comparison of H_{c_2} to T_c at 4.2°K (the ratio H_{c_2}/T_c may be taken as a useful index of the high magnetic field potential of a class of materials, as can be seen in Table V). In order to make this comparison it has been necessary to approximate H_{c_2} (4.2°K) for Mo_3Al_2C from H_{c_2} (1.2°K) and T_c (given in Table IV) with the theoretical temperature dependence of H_{c_2} (shown schematically in Fig. 3). The result is H_{c_2} (4.2°K) $\simeq$ 126-130 kG, i.e., almost the same as for niobium nitride, yet T_c for Mo_3Al_2C is much lower than that for NbN. As a useful guide, data for Nb_3Sn and for metallic solid-solution alloys are included. Since Nb_3Sn not only has the highest known T_c but also the highest known H_{c_2}, it serves well as the standard for comparison. That H_{c_2} (4.2°K)/T_c for Mo_3Al_2C compares favorably to that for Nb_3Sn is readily apparent (Table V), and both exceed the values for NaCl-type ceramic compounds.

CONCLUSIONS

A summary of the effects of the three structural variables on the three main superconductive properties is given in Table VI. Although microstructure per se has a large effect on J_c, microstructural studies are essential in all superconductivity investigations so that in multiphase alloys the measured T_c and H_{c_2} values can be attributed to the proper phase. A combination of optical microscopy, electron microprobe analysis, x-ray diffraction, impurity analyses and, perhaps,

electron microscopy are invaluable aids in the characterization of materials prepared for superconductivity studies. As an example, a photomicrograph of a specimen of W_3Re_2C (β-Mn structure), which had been hot-pressed in a graphite die, clearly showed a second phase (Fig. 12). The second phase could not be identified by x-ray diffraction analysis because the diffraction pattern for W_3Re_2C, which is complex, was inextricably intermixed with that of the second phase, and also, only a small amount of the second phase was present. Electron microprobe analysis indicated that the matrix (W_3Re_2C) contained both tungsten and rhenium, as it should, but that the second phase contained no rhenium (Fig. 13). The microhardness of both phases was found to be very high. It was concluded that the second phase was probably hexagonal W_2C, which is not superconductive above 4.2°K. Thus, the results shown in Table IV for W_3Re_2C seemed clearly to be for that compound rather than for the other phase present in the alloy.

With the exception of many NaCl-type ceramic compounds and a couple of β-Mn structure ceramic compounds, the magnetic field properties of ceramic superconductors are unknown. It is considered highly likely that there are many potentially useful but as yet undiscovered or discovered but not fully evaluated ceramic superconductors. Ceramists can very likely make significant contributions to this field through careful preparation, accurate microstructural analysis, and careful superconductivity tests of ceramic compounds.

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FIGURE CAPTIONS

Fig. 1 Representative variation of electrical resistivity as a function of temperature for high-purity normal metals and for two high-critical temperature superconductors.

Fig. 2 Ideal isothermal magnetization curves for a Type I superconductor (broken line) and for a Type II superconductor (solid line).

Fig. 3 Phase diagram for a Type II superconductor showing schematic temperature variation of the upper critical field (H_{c_2}) and the lower critical field (H_{c_1}).

Fig. 4 The effect of microstructural variation through cold work and precipitation on the critical current density (J_c) as a function of applied transverse magnetic field at 4.2°K for a 71Nb-29Zr alloy.[6]

Fig. 5 Critical current density (J_c) as a function of applied transverse magnetic field at 4.2°K for a 71 Nb- 29 Zr alloy in two microstructural states (heavy curves) and "design reference" curves for superconducting solenoids (light lines).

Fig. 6 Qualitative correlation of critical temperature as a function of valence electrons per atom for the elements (modified, after Matthias).[18]

Fig. 7 The composition dependence of critical temperature for B1 structure niobium carbide and tantalum carbide.[12]

Fig. 8 The composition dependence of critical temperature for B1 structure niobium nitride [O (Ref. 33), ● (Ref. 24), □ (Ref. 21), ▽ (Ref. 34), △ (Ref. 35).]

Fig. 9 The composition dependence of critical temperature for B1 structure niobium carbo-nitrides near stoichiometry (solid curve) [× (Ref. 38), O (Refs. 35,37).]

Fig. 10 The variation of critical temperature with valence electrons per metallic atomic volume for various B1 structure ceramic compounds and FCC alloys based on iridium.

Fig. 11 The composition dependence of upper critical field for B1 structure niobium carbo-nitrides near stoichiometry (solid curve). [x (Ref. 38), o (Ref. 35, 40).]

Fig. 12 Microstructure of hot-pressed W_3Re_2C (β-Mn structure) plus second phase [250x].[46]

Fig. 13 Electron microprobe display patterns of rhenium characteristic x-radiation (left) and of tungsten characteristic x-radiation (right) for specimen shown in Fig. 12.[about 1000x].[46]

TABLE I. Occurrence of Superconductivity

	Range of Critical Temperature
Elements	0 - 9.5°K
Metallic Solid Solutions	0 - 14.0°K
Intermetallic Compounds	0 - 18.1°K
Ceramic Compounds	0 - 17.3°K

TABLE II

Superconducting Properties of the Carbides and Nitrides with the NaCl Structure

Compound	Total valence electrons	T_c(°K)	Compound	Total valence electrons	T_c(°K)
Group III Nitrides			Group IV Carbides		
ScN	8	Normal*	TiC	8	Normal
YN	8	Normal	ZrC	8	Normal
LaN	8	Normal	HfC	8	Normal
Group IV Nitrides			Group V Carbides		
TiN	9	5.6	$VC_{0.88}$	8.5	Normal
ZrN	9	10.7	NbC	9	11.1
HfN	9	6.2	TaC	9	9.7
Group V Nitrides			Group VI Carbides		
VN	10	8.2	CrC	(10)	**
NbN	10	15.8	MoC	10	Exist at high temperatures only
TaN	(10)	**	WC	10	

*"Normal" means not superconducting down to about 1°K.
**Does not exist with NaCl structure.

TABLE III

Superconducting Critical Temperatures and Crystal Structures for Some Metastable Compounds

Compound	Equilibrium Structure	Rapid-Quench Structure
MO_3C_2*	Hexagonal 9.0±0.2°K	Cubic (NaCl) 13.0±0.5°K
MoC**	Hexagonal 9.3°K	Cubic (NaCl) ~12 - 14.3°K
WC**	Hexagonal Normal to 0.3°K	Cubic (NaCl) ~7 - 10.0°K

* Ref. 10.

** Ref. 11.

TABLE IV

Superconducting Ceramic Compounds of the Beta-Manganese Structure

Compound	T_c(°K)	H_{c_2}(kG)
Mo_3Al_2C*	10.0	156 (1.2°K)
W_3Re_2C**	7.1 - 7.3	53.5 (4.2°K)
Nb_3Al_2N***	1.3	----------

* Ref. 44, 45.

** Ref. 46.

*** Ref. 47.

TABLE V

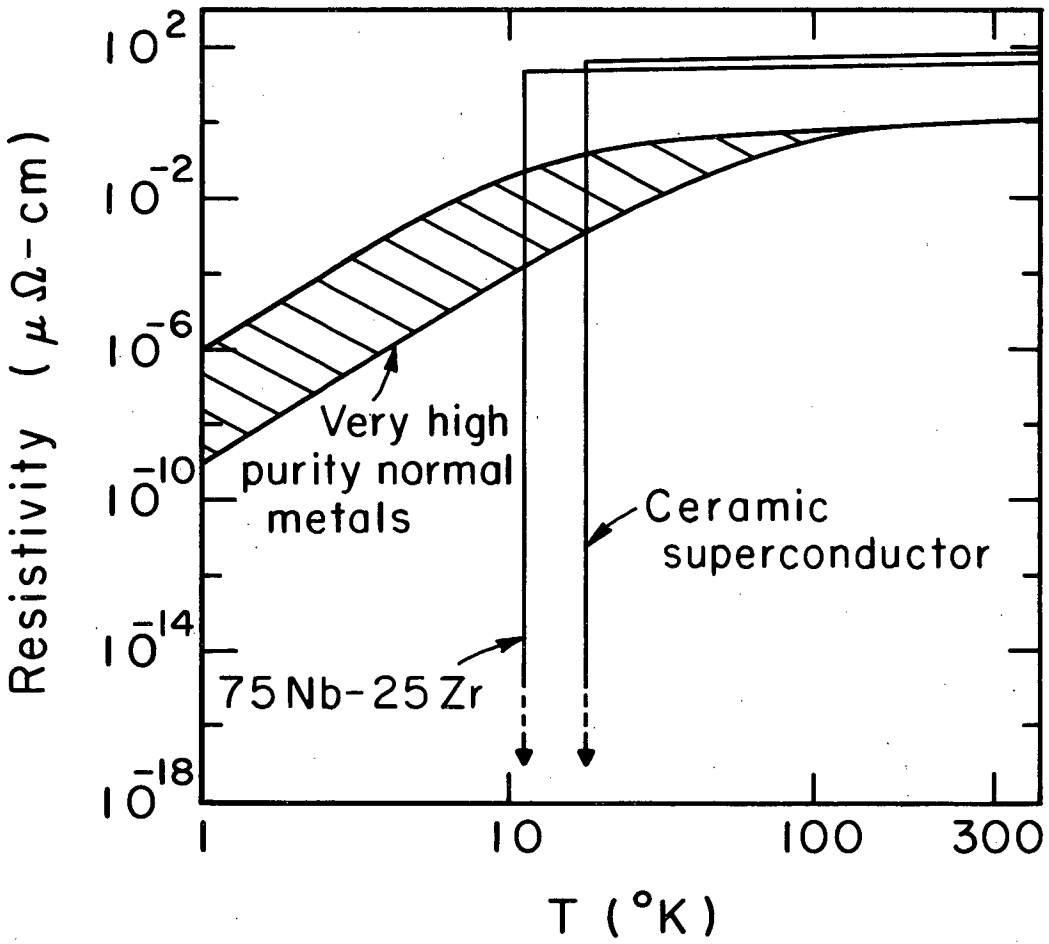
Comparison of High Magnetic Field Superconductive Materials

Material	H_{c_2}(kG) at 4.2°K	T_c(°K)	$H_{c_2}(4.2°K)/T_c$
75Nb-25Zr	70	10.9	6.4
45Nb-55Zr	96	10.2	9.4
60 w/o Nb-40 w/o Ti (56 a/o Ti)	115.5	9.2	12.6
Nb_3Sn	221	18.1	12.2
$NbN_{0.93-0.96}$	118	17.3	6.8
$NbC_{0.3}N_{0.7}$	114	17.8	6.4
Mo_3Al_2C	126-130	10.0	12.6-13.0

TABLE VI

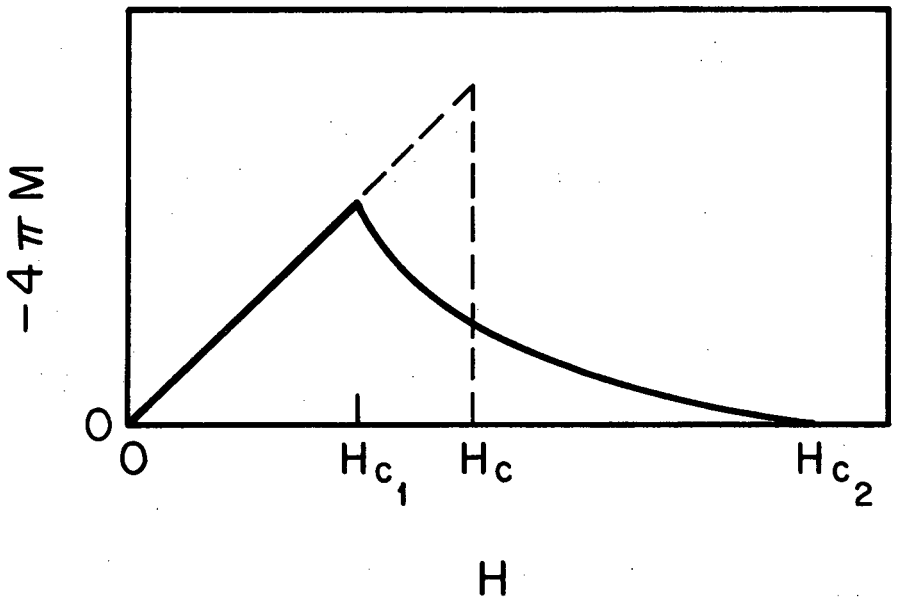
Effect of Structural Parameters on Superconductive Properties

Effect of → on ↓	Crystal Structure	Composition	Microstructure
Critical Temperature [T_c]	Large	Large	Negligible
Upper Critical Field [$H_{c_2}(T)$]	?	Large	Slight
Critical Current Density [$J_c(H,T)$]	Negligible	Slight	Large



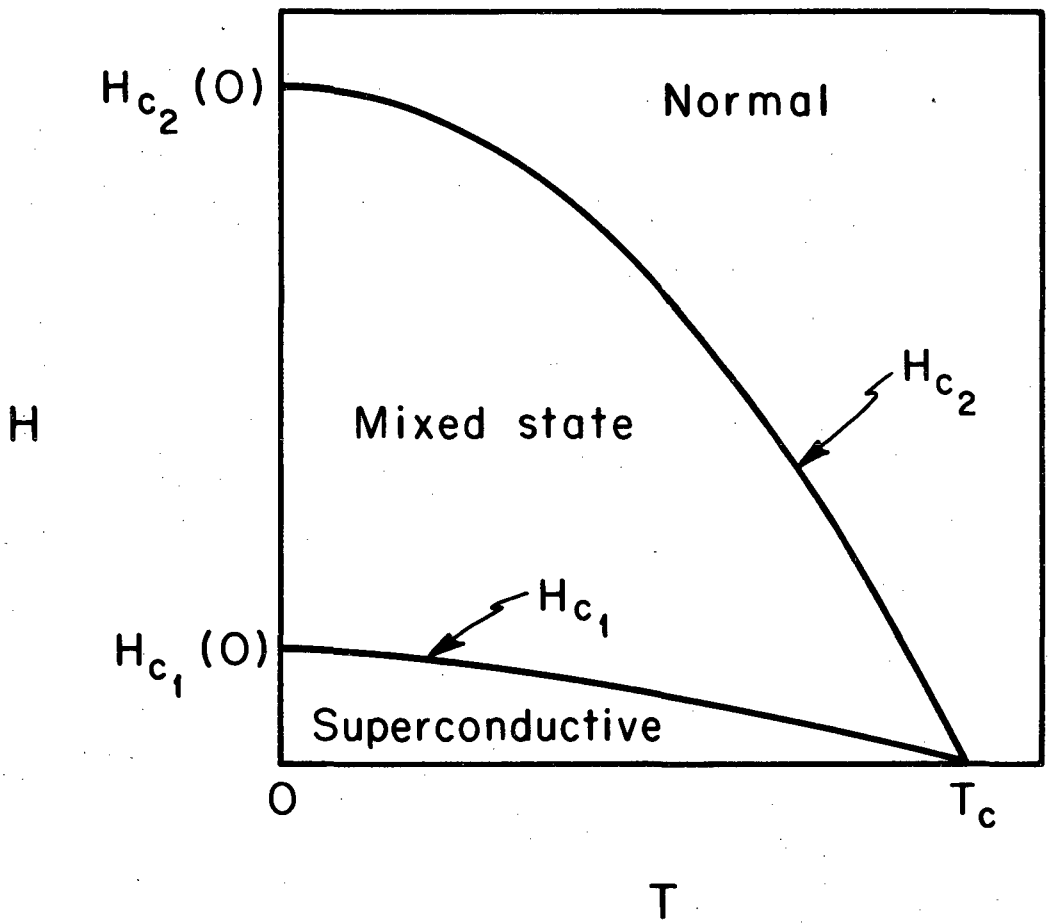
MUB-10490

Fig. 1



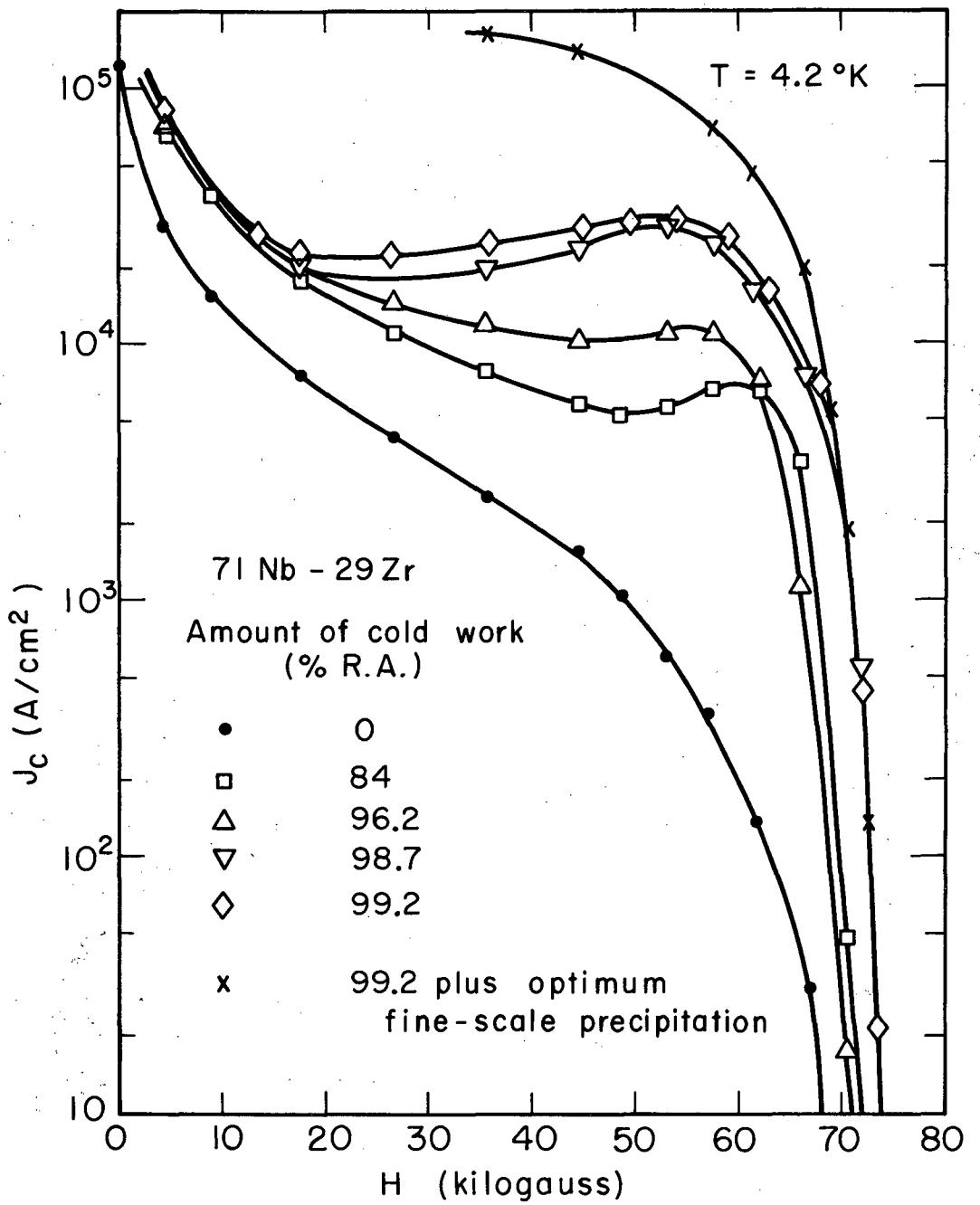
MUB 11628

Fig. 2



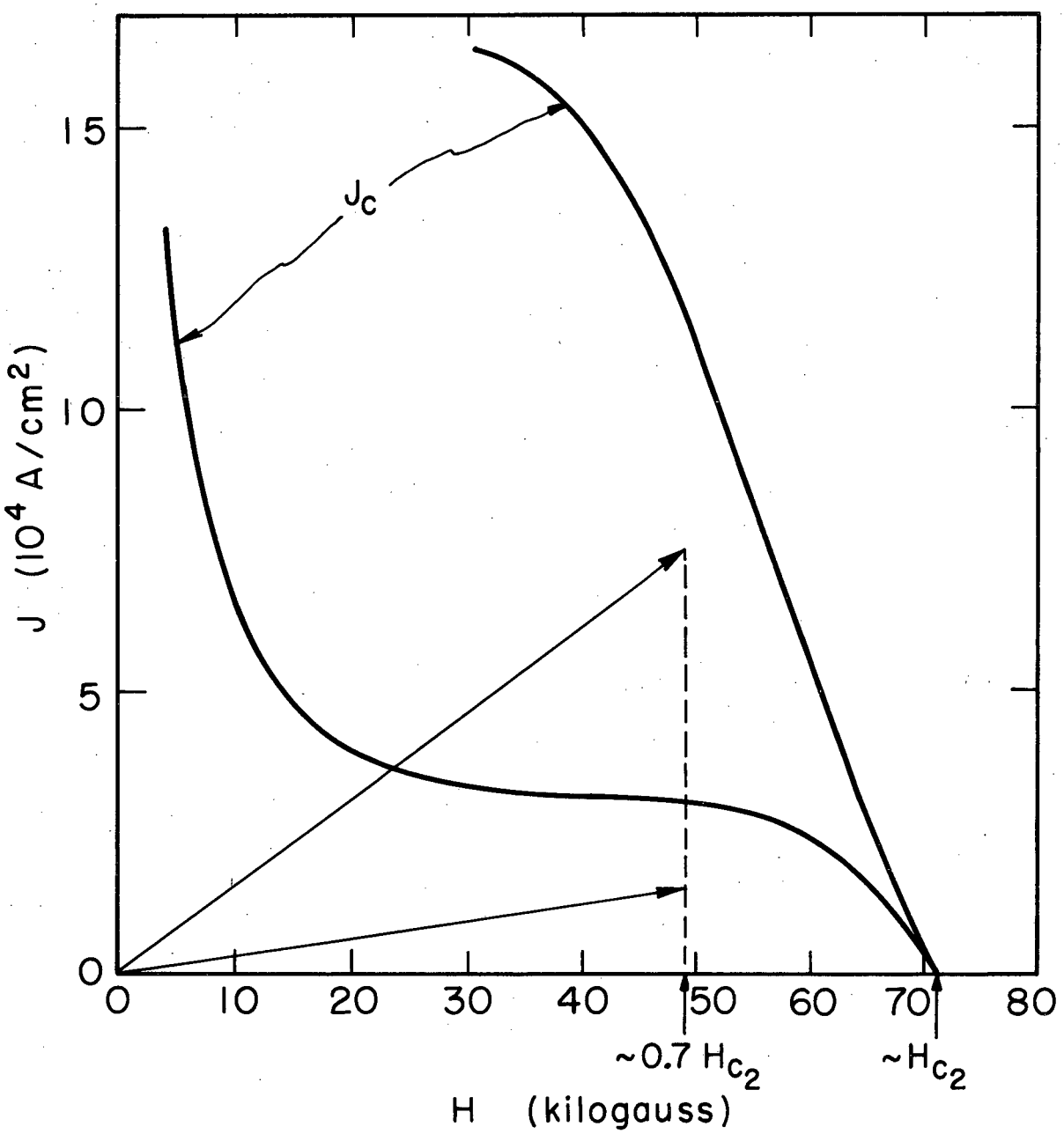
MUB 11626

Fig. 3



MUB-10716

Fig. 4



MUB-10715

Fig. 5.

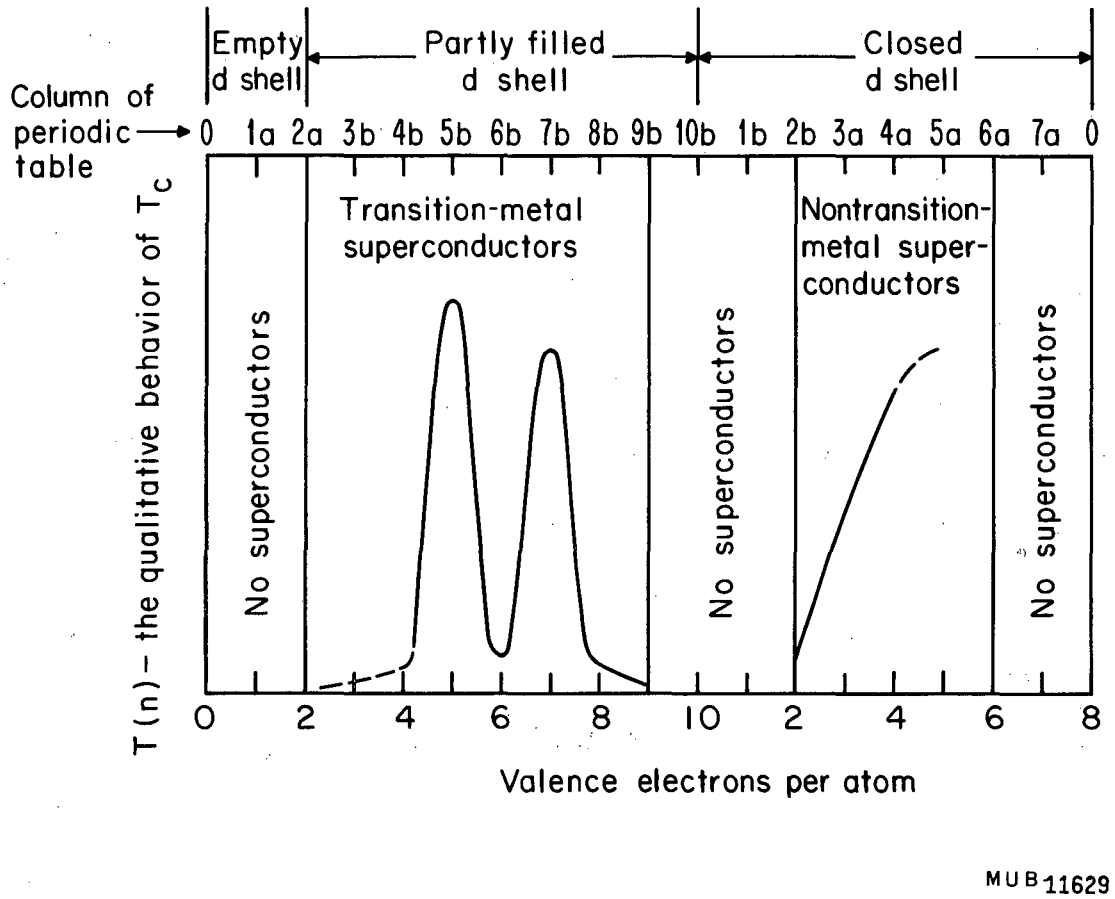
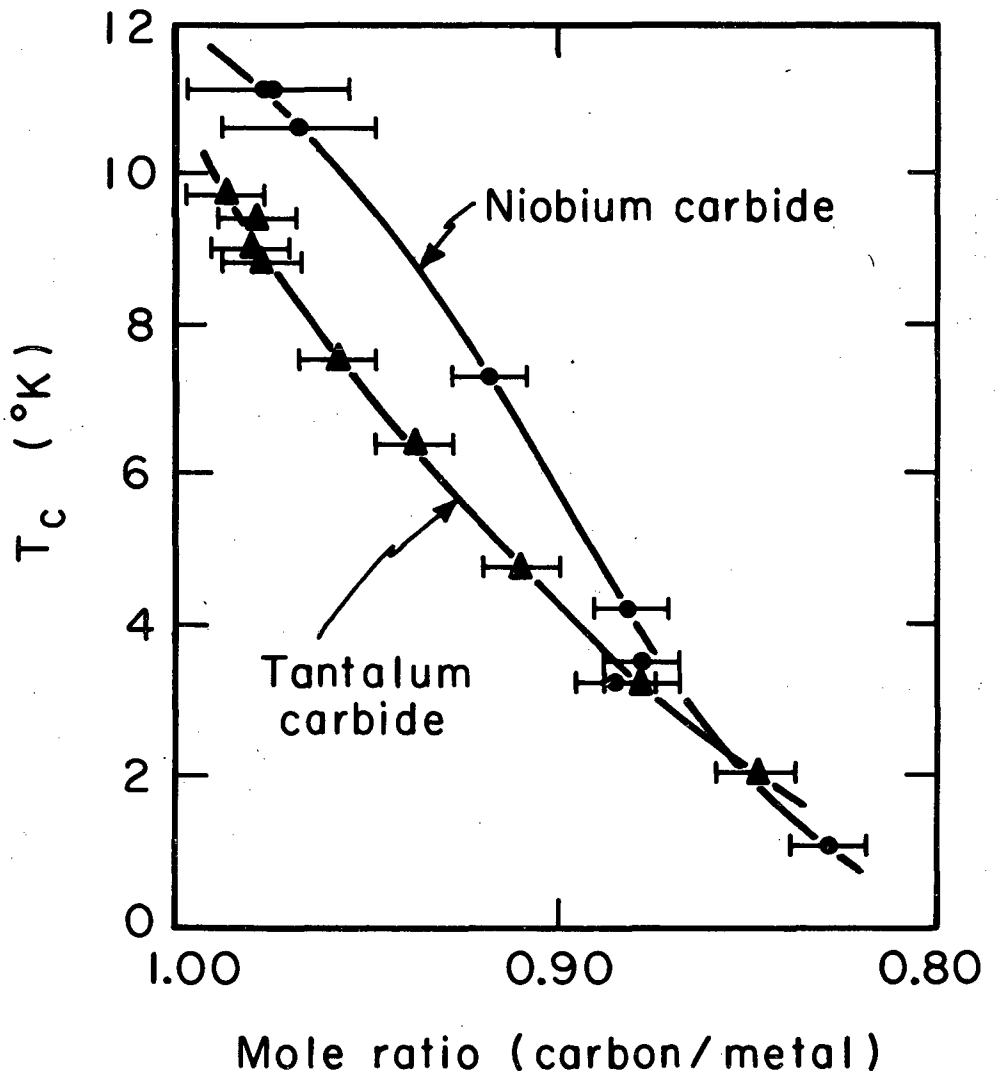
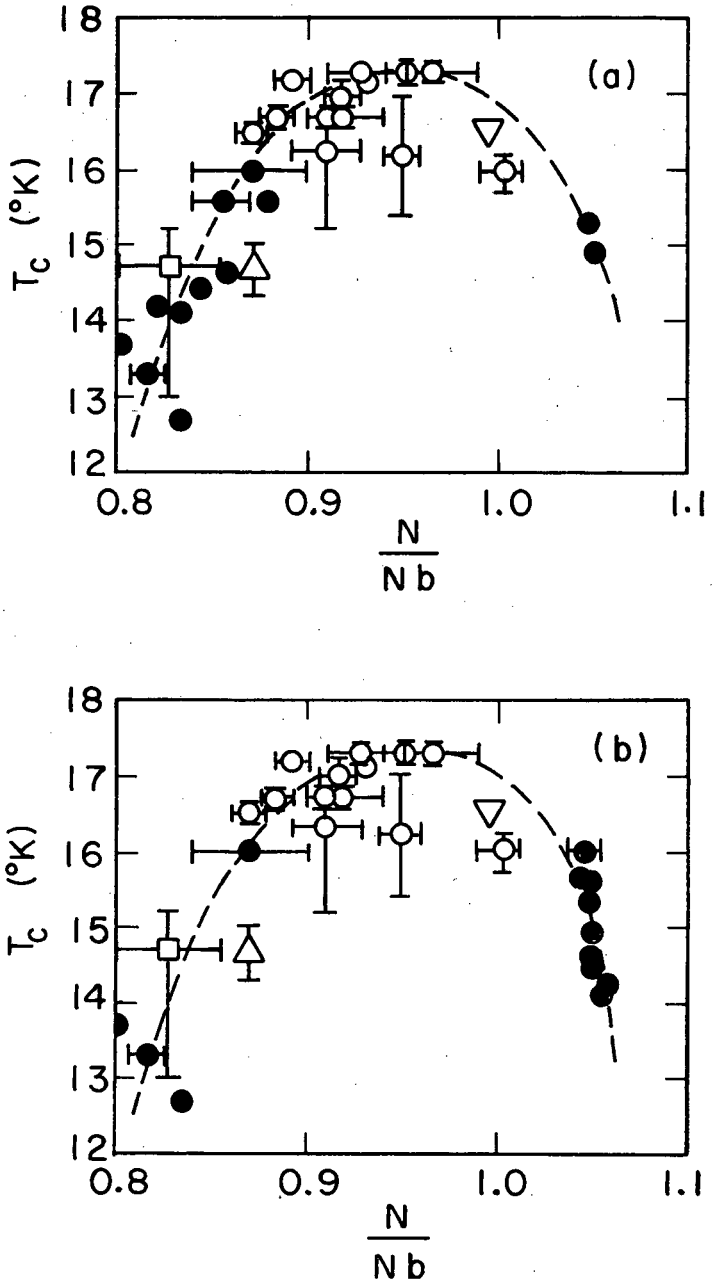

Empty d shell
Partly filled d shell
Closed d shell
Column of periodic table
0 1a 2a 3b 4b 5b 6b 7b 8b 9b 10b 1b 2b 3a 4a 5a 6a 7a 0
Transition-metal superconductors
Nontransition-metal superconductors
No superconductors
No superconductors
No superconductors
T(n) – the qualitative behavior of T_c
0 2 4 6 8 10 2 4 6 8
Valence electrons per atom
MUB 11629

Fig. 6.



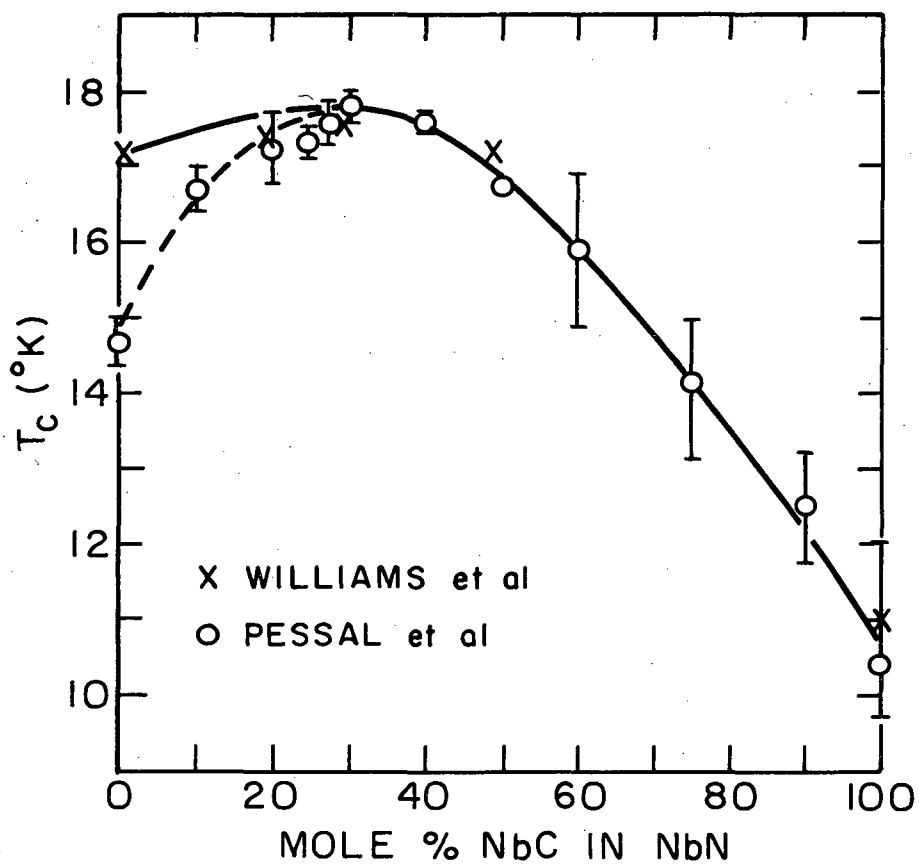
MUB-11627

Fig. 7



MUB-10013

Fig. 8



MUB-10444

Fig. 9

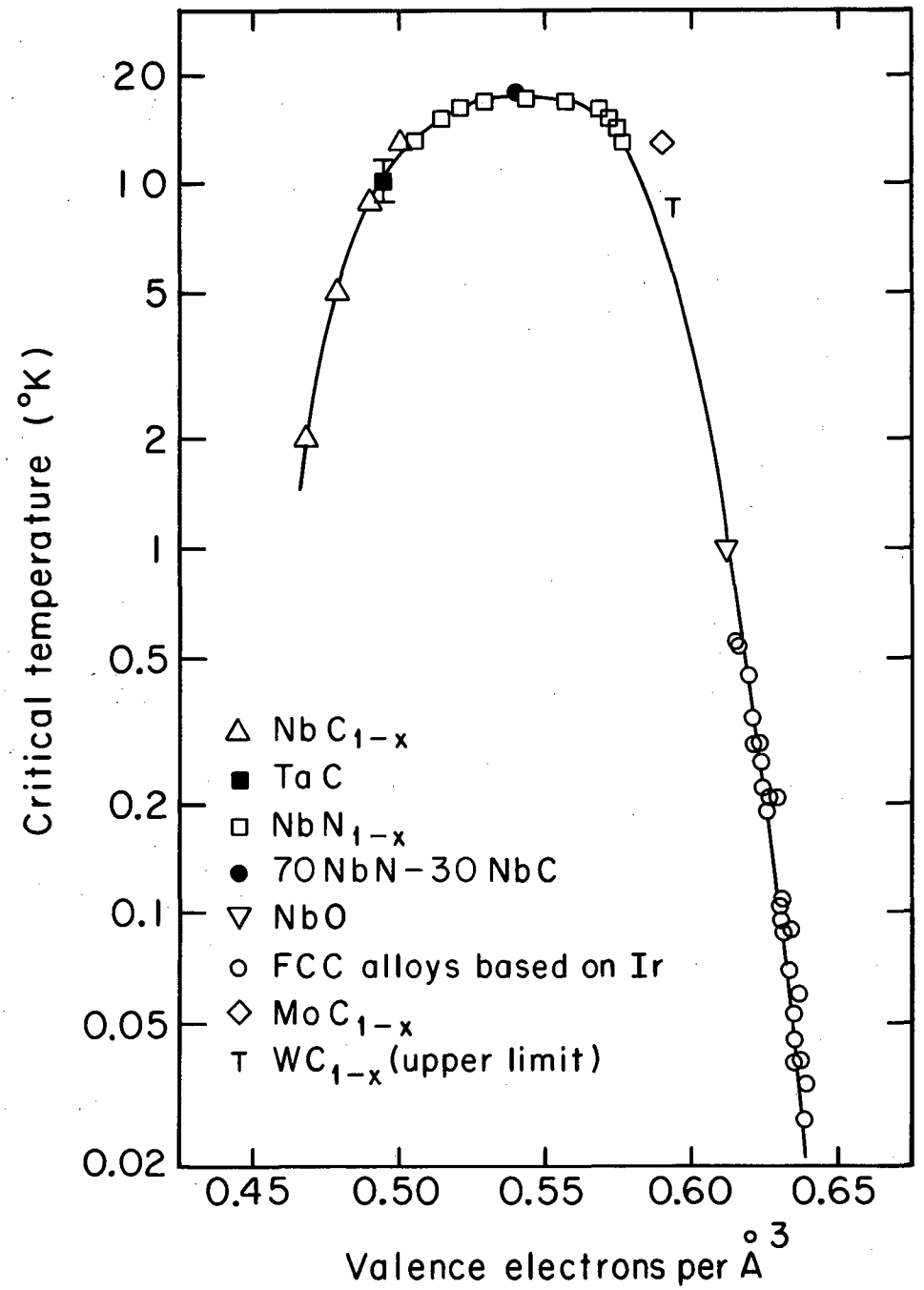
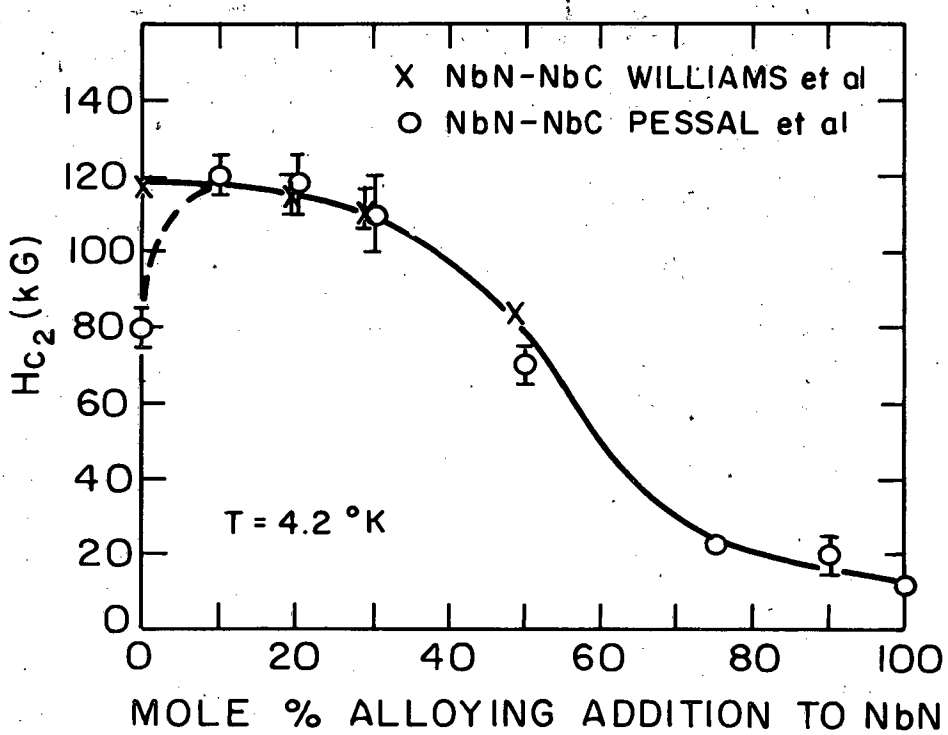
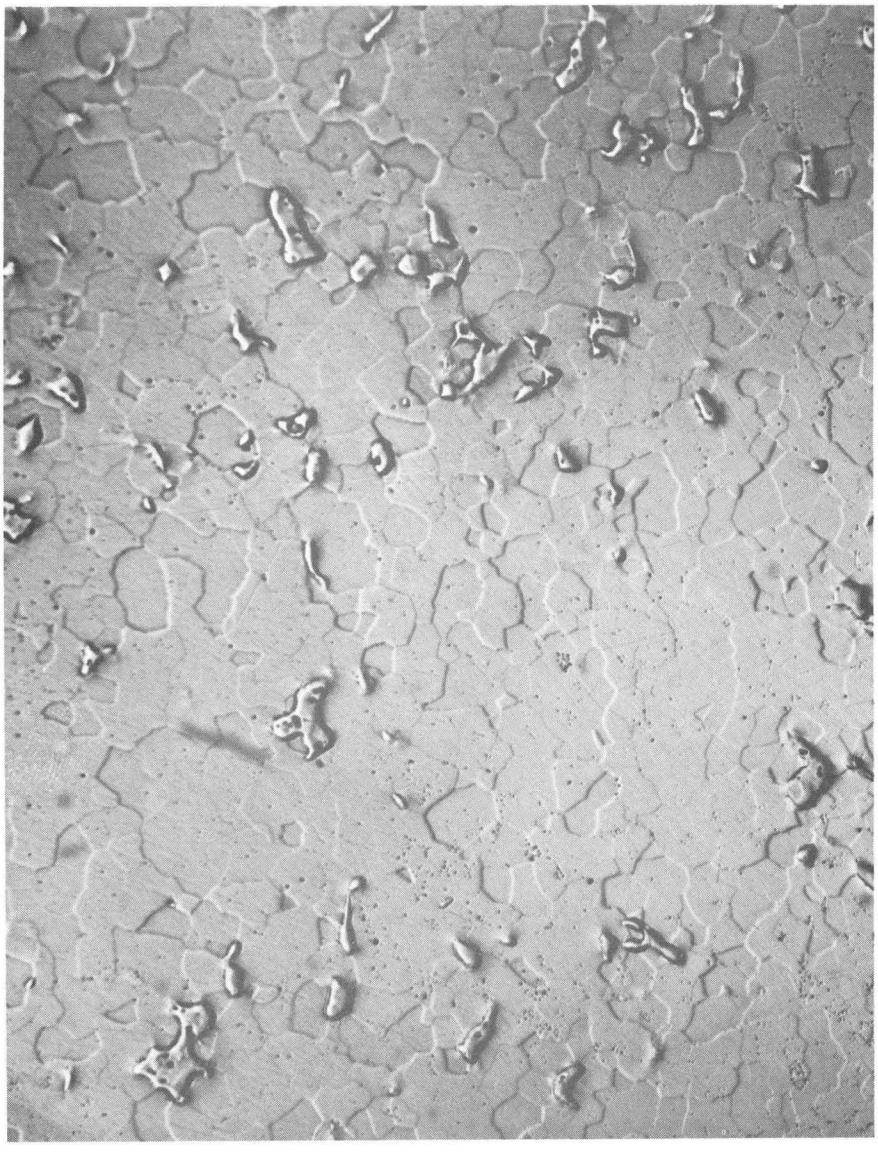

Critical temperature (°K)
20
10
5
2
1
0.5
0.2
0.1
0.05
0.02
0.45
0.50
0.55
0.60
0.65
Valence electrons per Å^3
Nb C$_{1-x}$
Ta C
Nb N$_{1-x}$
70 Nb N − 30 Nb C
Nb O
FCC alloys based on Ir
Mo C$_{1-x}$
W C$_{1-x}$ (upper limit)
T
MUB-10491

Fig. 10.



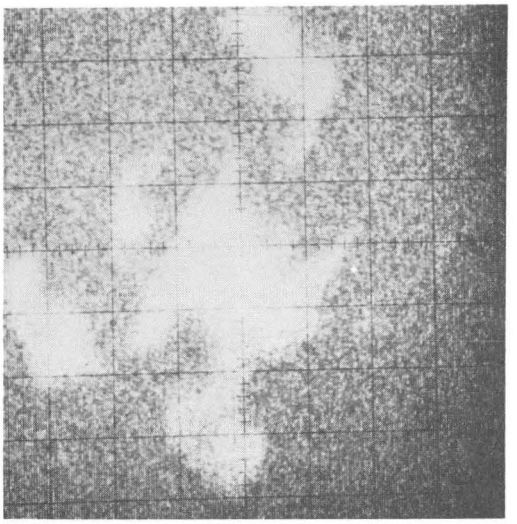
MUB-10443

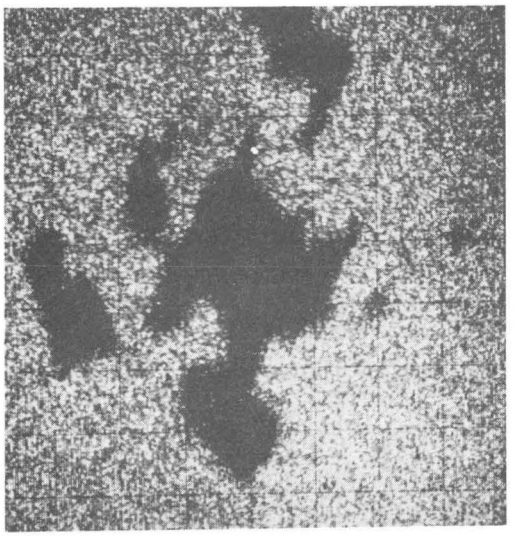
Fig. 11.



ZN-5817

Fig. 12.





ZN-5816

Fig. 13.

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