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Publication Date

1968-07-01

ey. 2

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Berkeley, California

UCRL - 18362 ey. 2

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UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California
AEC Contract No. W-7405-eng-48

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SUPERCONDUCTIVITY AND PHASE DIAGRAMS

V. F. Zackay[*], M. F. Merriam[*], and K. M. Ralls[**]

I.   INTRODUCTION

The positions of boundary lines on alloy constitution diagrams can be, and have been, determined by measurement of almost any physical property which varies with composition, by plotting the value of the physical property against composition and picking out the compositions where the plot departs from a smooth curve. The so-called "disappearing phase method" of using x-ray lattice parameter measurements to determine solid-solid phase boundaries[1] is an example of this. Other properties often measured include electrical resistivity, thermoelectric power and electrode potential.[2]

Superconducting transition temperature, T_c, is, in some systems, a very suitable property for determing phase diagrams in this way, for the following reasons.

1.   It (T_c) is extremely sensitive to changes in the electronic state of the metal. Such changes in electronic state (specifically, electron density of states at the Fermi Energy) always occur in association with crystallographic changes.

2.   It can be measured to good precision (1 part in 1000). Thus the position of the line on the phase diagram can be located unambiguously.

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3. Determination of T_c is a very easy measurement; the infinite conductivity is such a gross property that it can be readily and unambiguously detected with simple equipment, even in a rather small specimen. The specimen may be in practically any physical form -- ingot, wire, powder, sponge, scale, etc. It is not necessary to attach leads. Samples can be measured in sealed tubes, which is a very convenient way to eliminate stoichiometry problems and to protect reactive materials.

4. T_c is generally not very sensitive to dislocation density, grain size, internal stress, non-metallic impurities -- all the defects which are difficult to control from one sample to the next.

Limitations of superconductivity as a phase discrimination tool are fairly obvious:

1. The alloys investigated must be superconducting, preferably with T_c above 1°K.

2. The measurement is carried out at the cryogenic temperature. Thus, phase diagram features are always studied by measuring the properties of quenched alloys, and are affected if changes in the specimen occur during quenching.

3. Although superconducting T_c measurements are simple and quick to carry out when the necessary apparatus is set up and operating, the cryogenic apparatus itself requires some time and know-how to set up, and is not inexpensive, It also requires liquid helium, which is not available in some parts of the world.

To determine superconducting transition temperature one must (a) monitor the state of the sample to detect whether it is in the normal or superconducting state, and (b) measure the temperature. The three methods available to detect superconductivity are (1) the measurement of inductance of a coil or set of coils which contain the specimen, (2) the measurement of the voltage drop across a sample (wire or bar) through which a current is passed, and (3) measurement of heat capacity. The last is the most reliable, but is also by far the most work, and requires a large sample. Consequently it is rarely used. Detecting a voltage drop requires that the sample be fabricated as a wire or sawn bar and that ohmic contacts be made to it. Furthermore it has the disadvantage that a single filamentary path between the contacts can make the whole sample appear superconducting. Thus one must be quite careful with alloy preparation, and know quite a bit about the alloy system under investigation, to avoid misleading microstructural situations -- i.e. high T_c filaments.

The most common method used for detecting T_c is to note the sudden change of inductance of a coil or set of coils surrounding the specimen. This method, essentially a measure of the magnetic susceptibility of the sample as a whole, depends on exclusion of magnetic flux from the region of space occupied by the sample. One may have either one coil, with the specimen in the center, in which case the self-inductance is measured, or two (often coaxial), in which case the mutual inductance -- the current induced in one coil by a driving current in the other -- is influenced by the (super-conducting or normal) state of the sample. The influence occurs because ac magnetic flux, associated with the ac signal applied to the measuring coil, is excluded from the superconducting volume by the infinite conductivity

according to Lenz's law.*

Since the flux exclusion, and thus the inductance change, arises from the eddy currents generated in a very thin layer on the outside of the sample, a non-superconducting sample coated with a superconductor (as a lead-plated golf ball) will appear superconducting. Thus less than 1% of a superconducting phase precipitated in the grain boundaries of a non-super-conducting matrix can (in the worst case) make the whole sample appear superconducting; the classic case is $LaRh_5$.[4] Nevertheless, the inductance method is more reliable for samples of uncertain microstructure than the resistance method, presumably because superconducting shells are less common than superconducting filaments. If results from a bulk specimen are suspect because of uncertain microstructure, grain boundary precipitation, etc., the sample can be powdered and remeasured. This will usually eliminate the microstructure and give a result characteristic of the bulk material. However, the only certain bulk measurement is the calorimetric one.

The most common ways to measure temperature are to use resistance thermometry or vapor pressure thermometry, depending on the temperature range. Vapor pressure thermometry (measuring pressure of vapor over a boiling liquid in equilibrium with it) is restricted to $20.4-14.8°K$ (H_2); $4.2-1.2°K$

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* A changing magnetic field induces a current, the sense of this current is such as to oppose the change in field, and if the conductivity is infinite, the magnitude of the field associated with the induced current is sufficient to completely cancel the applied field. The observed sudden change of coil inductance at the transition has nothing to do with the Meissner effect. Since the infinite conductivity is the property detected, it is not important whether the sample is Type I or Type II.[3] The Meissner effect is the exclusion of _static_ magnetic flux from a sample when the sample enters the superconducting state, as on cooling. It is not a consequence of the infinite conductivity, nor is the infinite conductivity a consequence of the Meissner effect; the two are independent. For a more complete discussion of this point, see reference (3).

(He^4); and 3.5-0.3°K (He^3). In practice the He^4 range is by far the most convenient. A big advantage of vapor pressure thermometry is that the sample can be immersed directly in the boiling liquid, so that the thermometer is guaranteed to be at the same temperature as the sample. Resistance thermometers made from metal are insensitive in the superconducting temperature range. Semiconductors (carbon or germanium) are used instead. Carbon thermometers are inexpensive and readily available (it is usual to use a fractional watt radio resistor); germanium thermometers are more reproducible, i.e. they hold their calibration better. It is possible to measure T_c to 1 mdeg (10^{-3}°K) with these various types of thermometers.

The high sensitivity of T_c to changes in lattice conformation, ordering, anything which leads to electronic structure changes, arises from its exponential dependence on the density of electronic states at the Fermi surface. In one commonly quoted formula[3]

$$T_c \simeq 1.14\theta_D \, e^{-1/N_o V}$$

where θ_D is the Debye characteristic temperature describing the lattice vibrations, N_o is the density of electronic states at the Fermi energy, and V is a coupling constant describing the strength of the electron-phonon coupling which produces the superconductivity.

As composition is varied in an alloy system, the variation of T_c is usually dominated by N_o. As Fermi surface dimensions (N_o is proportional to Fermi surface free area) change with alloying, any discontinuity caused by shift in position of the zone boundaries (crystallographic phase change), new zone boundaries (ordering) or qualitative discontinuous change in Fermi surface shape ("electronic structure effects") will appear as discontinuities

or kinks in T_c, magnified by the exponential function. Thus the effect on T_c of a rather gentle martensitic phase transformation in In-Tl is easily visible.[5,6] An order-disorder transformation of unique type[7] was discovered in Hg-Cd through following up anomalous T_c measurements, and electronic structure effects in indium-based solid solutions[8-10] have been found and studied with superconductivity.

Because of the exponential dependence on density of states, T_c is likely to be a strong function of composition in any alloy phase. The technique of fixing phase boundaries by noting the composition at which a property ceases to vary with composition, is usually employed in connection with x-ray parameter measurements. However, T_c measurements are often more suitable, if not so universally applicable, because of the stronger composition dependence of the measured property. A phase boundary in Hg-In[11] was located in this way, when it probably could not have been by lattice parameter measurement.

II. PHASE DIAGRAM OF THE SUPERCONDUCTING STATE

The bulk of this chapter, and indeed of the entire book, is concerned with conventional phase diagrams which display the extent of each crystallographic structure, using temperature and composition as coordinates. However, this is not the only kind of phase diagram, since structure is not the only defining attribute of a state of matter, and temperature and composition are not the only thermodynamic variables which can be used as coordinates. It is common to display the superconducting state of a given material on a phase diagram of the sort shown in Fig. 1 where the extent of the superconducting state is shown as a function of magnetic field and temperature. The free energy of the electrons in a metal is, for low enough H and T (area under curve), lower when the electron gas of that metal is in the ordered (in momentum space) superconducting state. The total free energy of the metal is thus lower in the superconducting state, since it is the sum of several terms, one of which is the free energy of the electrons. Superconductivity is an ordering of the electron gas -- the other subsystems of the metal (lattice, nuclei) are not affected to the first order. Crossing the curve in Fig. 1 is thus a phase transition in the true thermodynamic sense. In general, it is a first-order phase transition, except at H = 0, where the latent heat of the transformation goes to zero. The phase transition can be treated thermodynamically, and various thermal and mechanical properties expressed in terms of the shape of the critical field curve.[3]

Superconductors can be classified as Type I or Type II.[3,12, 13] Type I superconductors are the pure elements (except Nb, and possibly V, Ta, Tc) and dilute alloys with less than a few percent impurity. Type II superconductors are those elements which are not Type I, all concentrated alloys, and

most compounds. For Type I superconductors the H - T curve is closely
parabolic

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

where H_c is the critical field at temperature T, and H_o is the value of H_c
at T = 0. For Type II superconductors the situation is more complicated.
It is a formidable experimental problem to prepare Type II superconductors
which show thermodynamically reversible behavior over the entire range of
the H - T curve. The "thermodynamic critical field" H_c is not the field at
which superconductivity vanishes, though it is related to this. No case is
known where the superconducting phase diagram does not have the general
appearance of Fig. 1 -- that is, where the superconducting phase field does
not surround the origin, or is not simply connected. The highest known T_c
is 20.04°K[14]; the highest known H_c, somewhat above 230 k oe.[15]

Superconducting H-T "phase" diagrams, like Fig. 1, are determined either
by placing the sample in a static field and finding the transition temperature
for various values of field, or by setting the sample temperature and varying
the field. In either case there are experimental pitfalls. A spatially
uniform magnetic field outside the sample does not imply a spatially uniform
field inside the sample, unless the sample is the right shape (a thin rod
parallel to the field, for a uniform field).

In a Type II sample, magnetic flux lines will only enter and leave the
sample in a reversible manner if the sample is extremely clean metallurgically
-- that is, free of defects which can pin flux lines. The transition tempera-
ture in zero field is not affected significantly by microstructural and lattice

defects, but the magnetic field required to destroy the superconductivity is. The critical field at various temperatures is often determined by measuring a magnetization curve-- magnetic moment is measured as the field strength is increased, and for Type I superconductors, drops suddenly to zero at H_c. If the same magnetization curve is traced out in decreasing or in increasing fields, reversibility is established and the thermodynamic superconducting phase diagram can be determined. As mentioned earlier, it is very difficult to prepare Type II materials to be magnetically reversible, and as a consequence, very few reliable superconducting phase diagrams for Type II materials exist.

Since the most technologically interesting superconductors are likely to have a considerable portion of their critical field curves (the line between superconducting and normal regions in Fig. 1 is often called the critical field curve) above 100 kilogauss, a substantial magnet apparatus is necessary. There are essentially three approaches: (1) a massive, water-cooled copper magnet, as a National Magnet Laboratory, Cambridge (USA); (2) a superconducting solenoid; or (3) a pulse magnet. The copper solenoids consume vast amounts of power and represent a major engineering task, but give the highest steady state fields (up to 250 kgauss, though most installations do not exceed 100 kilogauss). Superconducting solenoids are much less expensive and produce fields to 140 kilogauss, though again, 70 or 80 kilogauss is a more common upper limit. Pulse magnets go to 500 kgauss, or even higher, and are the only practical alternative for many laboratories; however, they are not without their problems. If the pulse duration is too short, very large eddy currents will be induced in the sample, leading to a critical field under pulse conditions which is much lower than the steady-state value. An

analysis of this situation has been made by Boyd.[16] In general the pulse

length must be at least milliseconds if the results are to be realistic above

100 kilogauss. Pulse magnets are unsuitable for determining precise equilibrium

superconducting phase diagrams.

A method for partially overcoming the problem of irreversibility by

flux pinning in metallurgically imperfect samples is to hold the field constant

and vary the temperature. The flux lines thus do not move and irreversible

motions do not occur. Provided the flux lines were in their equilibrium

configuration to begin with, and the transition is detected in some manner

(ideally calorimetrically) which does not disturb them, the correct H_c can in

principle be obtained.

III. SUPERCONDUCTIVITY AND THE DETERMINATION OF PHASE DIAGRAMS

The preceding sections have described how the superconductive transition, i.e. the change from the superconducting to the normal state, is a phase transition in the true thermodynamic sense and, also, how several superconducting properties are highly dependent upon either structure or composition or both. Further, it has been shown that the superconducting transition temperature is readily measured. These observations suggest that the property of superconductivity is likely to become an important tool in the determination of phase diagrams. That this has not yet been realized is largely due to the fact that the principle effort to date has been directed toward the discovery of new and, hopefully, superior superconductors. Nevertheless, sufficient evidence already exists in the published literature to illustrate how superconductivity can be used to increase substantially our understanding of the equilibrium and non-equilibrium properties of metallic and ceramic solids.[*] The recent critical review by Ralls et al.[17] on the superconductivity of ceramic compounds is recommended to readers desiring more detailed treatment of this subject.

Although there have been significant advances in the theory of superconductivity since its discovery at the turn of the century, it is not yet possible to predict from theory alone either the occurrence or the strength f of superconductivity. Thus, we must rely upon empirical guids, the most important being those first proposed by B. T. Matthias.[18-20] These are,

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[*] All superconductors are metallic, in the electronic sense, at temperatures just above T_c -- a phase transition in the electron gas, which is what superconductivity is, is only possible if there is an electron gas -- but some are ceramic in the mechanical or chemical sense.

briefly, (1) certain crystal structures are favorable for the occurrence of superconductivity; and (2) the critical temperature is a systematic function of the number of valence electrons per atom.

The qualitative correlation of critical temperature (T_c) with the number of valence electrons per atom (e/a), as shown in Fig. 2, has widespread validity for elements, metallic solid solutions, and, to some extent, inter-metallic compounds. Counter examples can be cited, but the correlation holds perhaps 90% of the time. 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 both 5 and 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 be included. On such a basis the maximum in T_c occurs at the commonly observed e/a ratio of about 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, as shown in Table I.[17]

We might expect, from the data of Table I, that MoC and WC, which exist with the NaCl structure only at high temperatures, would have high critical temperatures. These compounds can be retained in the NaCl structure by rapid quenching. As shown in Table II, 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. Although this investigation of the superconductive properties of MoC and WC was initiated to investigate the Matthias correlation for ceramic compounds, it eventually led to an improved understanding of the relationship between the cubic and hexagonal forms of

these compounds.

It is well known that intermetallic and ceramic compounds can exist over a wide range of homogeneity. The deviation from stoichiometry, often too small to be detected by chemical means, is frequently reflected in inexplicable variations in physical properties. Superconducting transition temperature can be very sensitive to stoichiometry, more sensitive than any chemical analysis. The classic cases are those of niobium carbide and tantalum caribde investigated by Giorgi et al.[21] As shown in Fig. 3, a change of about six atomic percent carbon in niobium carbide altered the T_c from below $1°K$ to over $11°K$. Giorgi et al. have also correlated the critical temperature of these compounds with the lattice parameter as a function of composition.

The relation between critical temperature and the deviation from stoichiometry for several compounds and solid solutions, all either of the NaCl or FCC structure, can best be portrayed by a plot of the critical temperature vs the number of electrons per unit volume, as shown in Fig. 4. The solid line in this plot is drawn through data points for stoichiometric compounds and solid solutions and the dotted lines through data points for compounds deviating from stoichiometry. In all cases data points for compounds deviating from stoichiometry lie on a branch curve of the envelope curve (solid line). Master curves such as these will undoubtedly prove useful in establishing the precise composition of ceramic and metallic compounds and solutions.

Pessall and Hulm[22] have studied extensively the superconducting properties of pseudo-binary and ternary interstitial alloys. The transition temperature-composition relationships for several systems having the NaCl-type structure are shown in Figs. 5 and 6.

Small amounts of gaseous impurities in transition metals often have a

dramatic effect on the electronic structure of the metal, and thus on T_c.

For example, the effect of nitrogen, oxygen, and carbon on the T_c of Ta is

very pronounced.[23-26] It was the attempt to understand the origin of this

very pronounced effect on T_c that led to the important discovery that the

nitrogen dissolved in Ta is crystallographically ordered, even at very small

concentrations. Thus, $Ta_{27}N$ is a compound, with characteristic Laue spots,[26]

not a disordered solid solution. Similarly, ordering occurs with carbon as with

nitrogen, at the composition $Ta_{64}C$.[27] The ordering splits the Brillouin

zone, introducing an extra energy gap. This necessarily cuases a rearrange-

ment of electron states and shifts the Fermi energy, though perhaps not a

great deal. The density of states can be a rather rapidly varying function

of energy in transition metals, and so even a small shift in Fermi energy may

result in a substantial change in density of states at the Fermi energy, the

quantity on which T_c is exponentially dependent. Usually the effect of

gaseous impurities is to depress T_c, but it is not clear that this need

necessarily be the case. Perhaps the puzzling case of technetium,[28-31]

where the transition temperature measured on the earlier, less pure, samples

was several degrees higher than that found later, can be explained as due to

dissolved atmospheric gases. Hardy and Hulm[32] found that the transition

temperature of TiN and VN are affected by the presence of oxygen whereas that

of ZrN is not. Additions of 25-30 atomic percent NbC to NbN raise the critical

temperature of the binary system to a high of 17.8°K.[33] Williams et al.[34]

in their study of this system contend that "pure" near-stoichiometric NbN

(low in oxygen) has a T_c of 17.2°K, i.e., one nearly as high as that found

by Matthias et al.[33] for $Nb(C_{0.30}N_{0.70})$. By virtue of the large effect of

small amounts of interstitials on the transition temperature, the ceramist is

thereby able to use superconductivity as a probe into the structure and composition of this and other important classes of non-metallic compounds.[17]

There have been several recent review papers[35-38] on the relation between superconducting properties and metallurgical factors. Both Matthias et al. [35] and Wernick[36] have discussed the advantages accruing from the coupling of metallurgical phase diagram studies with the search for new super-conductors. The relative effects of structural and compositional factors on superconducting properties of both metals and ceramics can be summarized as shown in Table III. The knowledge and application of these relationships will undoubtedly play a role in the phase diagram determinations of the future.

ACKNOWLEDGMENT

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Fig. 1

XBL 6S6-994

Fig. 2
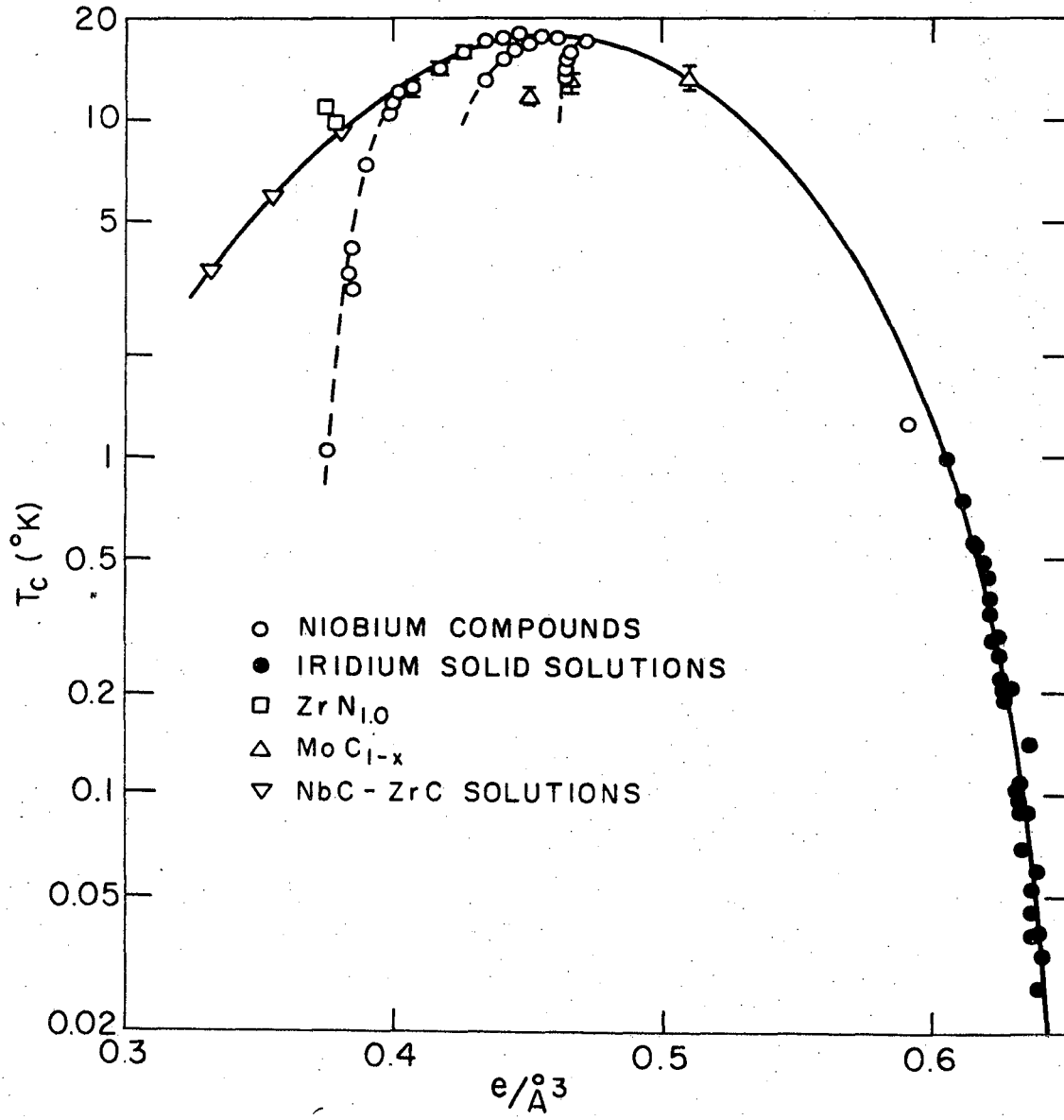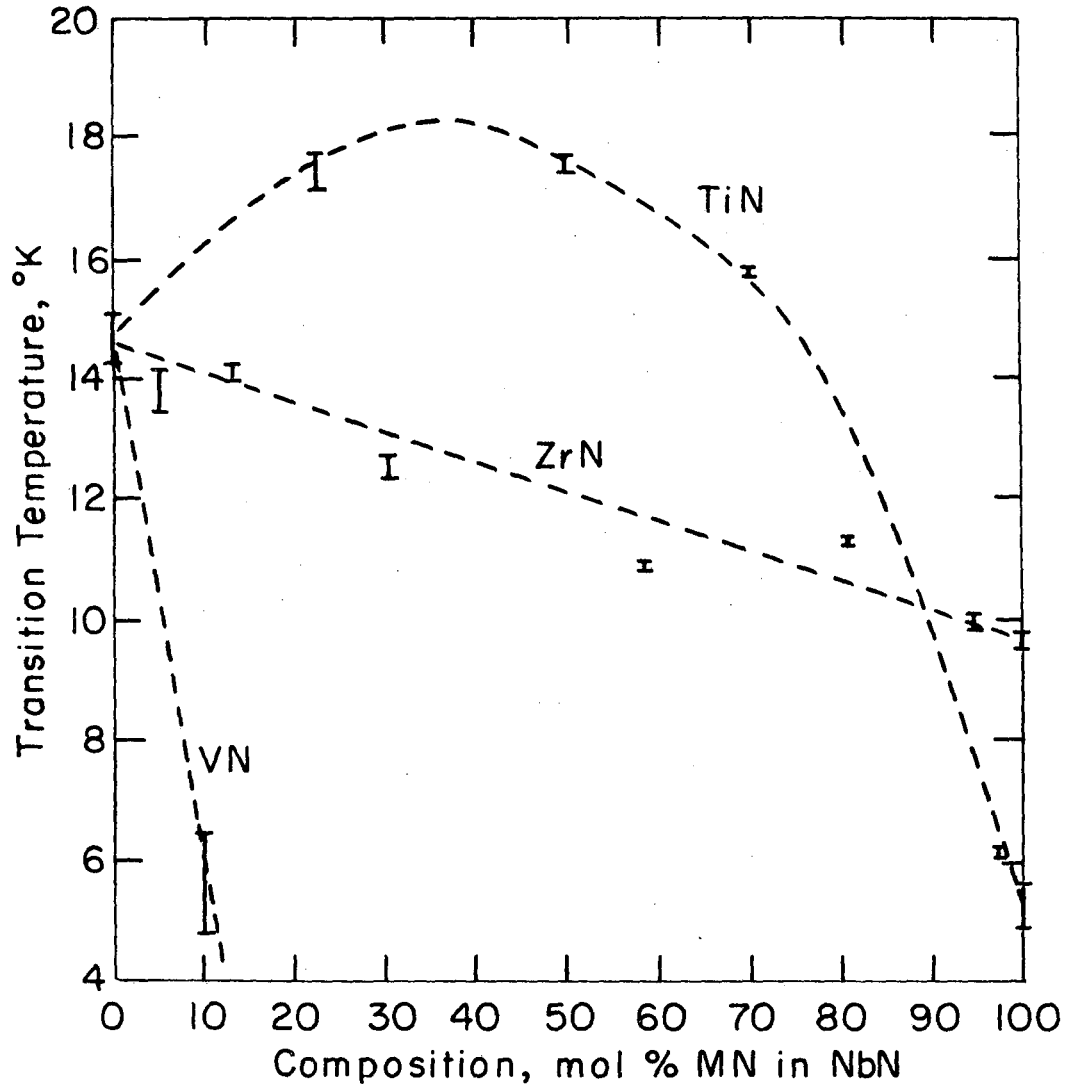
Fig. 3

Fig. 4

Fig. 5

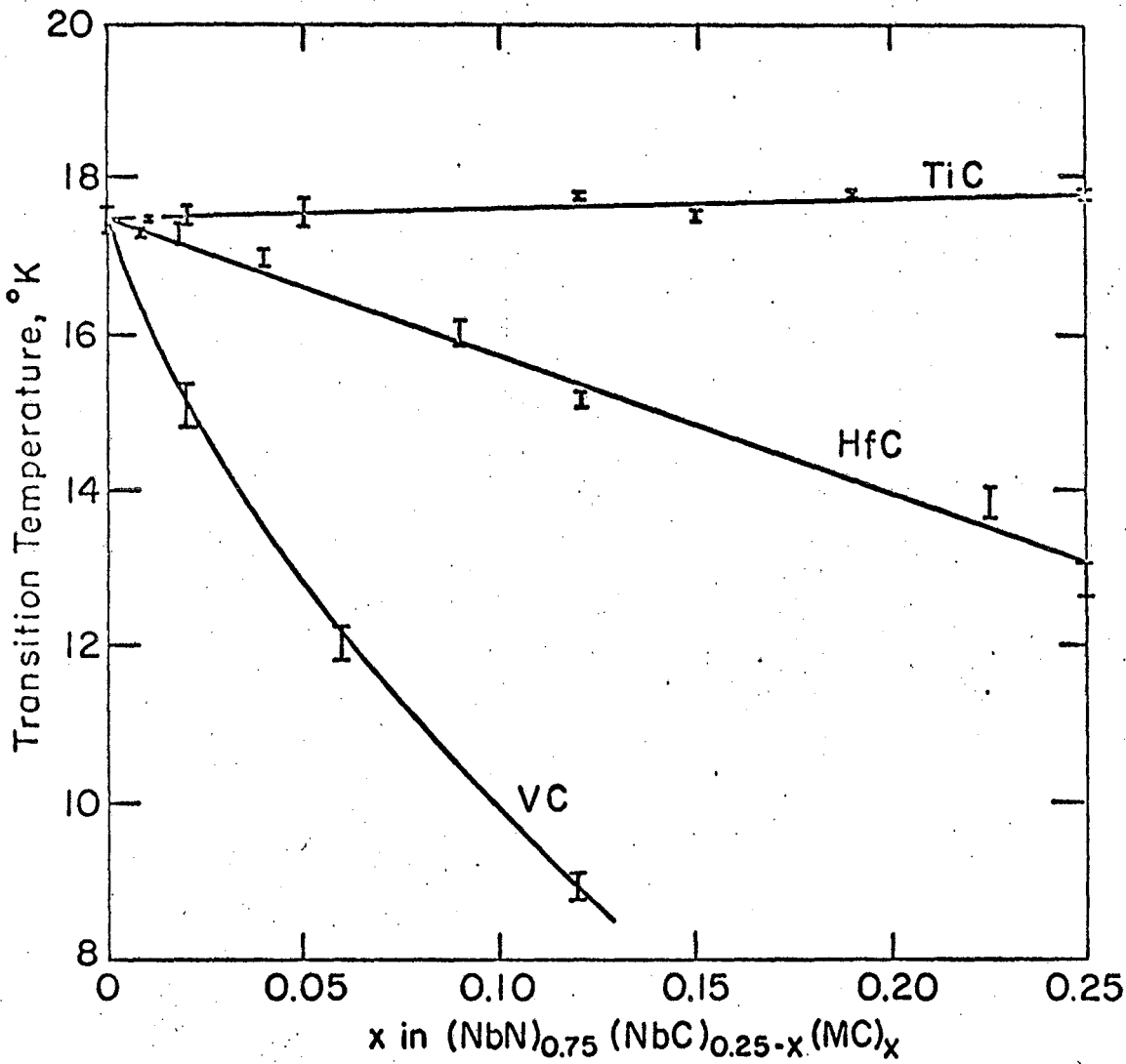Fig. 6

XBL 687-1176

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.

SUPERCONDUCTING TRANSITION TEMPERATURES AND 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
Mo C**	HEXAGONAL 9.3°K	CUBIC (NaCl) ~12 – 14.3 °K
W C**	HEXAGONAL NORMAL TO 0.3°K	CUBIC (NaCl) ~7 – 10.0 ° K
Nb_3Al**	CUBIC (A15) 18.0 °K	CUBIC (bcc) 3.1 °K

* TOTH et al
** WILLENS AND BUEHLER

Effect of → on ↓	Crystal structure	Composition	Microstructure
Critical temperature $[T_c]$	Large	Large	Negligible
Upper critical field $[H_{c2}(T)]$	?	Large	Slight
Critical current density $[J_c(H, T)]$	Negligible	Slight	Large