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INVESTIGATION OF HIGH FIELD SUPERCONDUCTING COMPOUNDS

Zelma Johnston Olson

May 1967

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INVESTIGATION OF HIGH FIELD SUPERCONDUCTING COMPOUNDS

Zelma Johnston Olson

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

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ABSTRACT

Only three β-Mn structures (interstitial compounds) are known to be superconductors, two of which were discovered at Berkeley. Compounds of this type appear to have excellent potential as high-field materials, when judged by a comparison of upper critical field to transition temperature. A review of the crystal structure and superconductivity of β-Mn structure compounds is presented here along with a report of the discovery of a new superconductor in this structure (the third of the group mentioned above). The new compound is W_3Re_2C, which has a T_c of 7.4°K. A discussion of the electron-to-atom ratio as applied to these filled interstitial alloys is also included.

The behavior of commercial hard superconductors is extremely sensitive to microstructure and the improvement of superconducting properties of transition metal alloys by controlled microstructure has recently become very important. A study of the effect of microstructure in two phase compounds and alloys of transition metals is presented. One result has been the synthesis of a two phase high-field superconductor with filamentary microstructure (Nb_3Sn in a NbC matrix, critical field higher than 200 kG at low current densities). A second significant accomplishment was the increase of the superconducting transition temperature of Ta-50 pct. Zr alloys by controlling the formation of the precipitate within the miscibility gap composition range of the Ta-Zr system.

I. INTRODUCTION

The effect of metallurgical variables on superconducting properties of materials has recently been reviewed by Livingston and Schadler.[1] They divide most superconducting properties of a given phase into three types; primary, secondary, and tertiary, in order of increasing structure sensitivity. This classification is schematically represented in Fig. 1.

The primary superconducting properties are (1) the critical temperature T_c, and (2) the thermodynamic critical field at absolute zero, H_o. These properties can be directly related to the Debye temperature θ, the density of states at the Fermi surface, (represented by the electronic specific heat coefficient γ), and the electron-electron interaction parameter V. The variations of T_c and H_o with concentrated alloying are related mostly to changes in γ, V, and θ with alloying, and not to the metallurgical structure.

For an alloy, the equilibrium properties in a magnetic field are strongly influenced by the mean free path ℓ, which can be determined from the normal resistivity ρ_n. Thus the various critical fields H_{c1}, H_{c2}, and H_{c3} are classified as secondary superconducting properties, as they are structure-sensitive to the degree that they depend on the mean free path ℓ.

Both primary and secondary properties relate to equilibrium behavior. The tertiary superconducting properties are those properties specifically relating to non-equilibrium behavior, which are controlled by the inhomogeneous nature of the sample. It is these tertiary or irreversible superconducting properties which determine the material's utility as a "hard superconductor" (i.e., a superconductor which is

capable of supporting high current densities in high magnetic fields). It is only within the last six years with the discovery of "hard superconductors", that any large-scale commercial utilization of the phenomenon has been visualized.

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 magnitudes of the primary superconductive properties. Thus it is necessary to rely upon empirical guides, the most important of which were first proposed by B.T. Matthias.[2,3] 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.

The crystal structure of known superconductors has been a useful guide in discovering others. The classic example is the large number of superconductive β-tungsten structure compounds. Other crystal structures such as the Laves phases and the X-phase or α-manganese structure show a pronounced tendency to be superconductive. The electronic structure of the alloy or compound is the primary superconductive property while the crystal structure is thought to have only a secondary influence. Yet, specific crystal structures appear again and again in the successful superconduction of technology.

The sensitivity of superconductive properties to the state of a material is most pronounced in a system when T_c varies with composition. Compositional inhomogeneities can affect T_c, provided the scale of the inhomogeneity is large enough. Where two phases or more are present in significant amounts, the measured critical temperatures are apt to be

influenced by measuring techniques and metallurgical structure.[4]

In this investigation we have searched for new superconductors, using empirical considerations such as crystal structure and electron-to-atom ratio, and have examined the effects of two-phase microstructures on equilibrium superconductive properties of compounds and transition metal alloys.

II. PROPERTY MEASUREMENTS

Microstructural changes were studied by x-ray diffraction, optical microscopy and electron beam microprobe analysis. X-ray diffraction studies were made with nickel-filtered copper Kα radiation (λ = 1.542Å) in a scanning diffractometer. The approximate lattice parameters were determined from low-angle diffraction peaks.

Superconducting-normal transitions of all samples were determined by observing the change in impedance of a coil operating at a frequency of one kH_z. The method employed was, in principle, similar to that of Merriam and Von Herzen.[7] The signal from the coil was amplified, detected and applied to one axis of an x-y recorder. The other axis was the voltage from a calibrated germanium thermometer. The midpoint of the transition was chosen as the transition temperature, although the beginning and the end of the transition have also been tabulated for all samples.

Resistive transitions from the superconducting to the normal state were measured in a high field pulsed magnet with the specimen at various current densities and at constant temperature (i.e., liquid helium temperature, 4.2°K). The experimental method is similar to that employed by Berlincourt and Hake.[8] The ends of "spark-cut" or "wire-cut" samples were ultrasonically tinned with indium and then soft-soldered to current leads. Voltage connections were made by pressure contacts approximately 0.5 cm apart. The pulsed magnetic field was applied perpendicular to the current flow through the sample. The voltage across the specimen and the current through a previously calibrated pulsed-field coil were displayed simultaneously on a dual beam oscilloscope and were recorded with high-speed Polaroid film. The critical magnetic field is taken as that field which leads to completely normal behavior (H_{rN}) at low current densities (about 20 A/cm^2).

A FAVORABLE CRYSTAL STRUCTURE

The exact effect of crystal structure on superconducting properties is hard to determine. It has been agreed for some time that certain crystal structures, e.g., b.c.c. structures for elemental superconductors,[1] β-tungsten structures for intermetallic superconductors,[2] seem to be favorable for the occurrence of superconductivity. The β-manganese structure has been shown to be a favorable crystal structure for the occurrence of superconductivity with outstanding high field characteristics in at least one instance. Mo_3Al_2C, the first known superconductor to form in the β-Mn structure, has a critical temperature of 10°K[9] with an upper critical field of 156 kG at 1.2°K.[10] The ratio H_{c2} (at 4.2°K)/T_c, which may be taken as a useful index of the high magnetic field potential of a class of materials,[11] compares quite favorably with that of Nb_3Sn (which has the highest known H_{c2}). Therefore a general survey of compounds crystallizing in the β-Mn structure has been undertaken.

The β-Mn structure is considered to be an electron compound requiring approximately 2s, p electrons per atom[12] or 7 electrons (i.e., total number of electrons outside a closed shell) per atom for the transition elements.[13] Thus the majority of the compounds forming in this structure contain at least one of the magnetic elements (i.e., Cr, Mn, Fe, Co, or Ni) and are therefore of little interest to superconductivity because of the complementarity between the occurrence of superconductivity and magnetism within the transition series.[14] But recently Nowotny's group and others[15-18,20,21] have observed the β-Mn structure in ternary carbides and nitrides of the group V and VI transition metals (i.e., Nb, Ta, Mo, etc.).

Structurally, Jeitschko, et al.[15] have shown the complex carbides of formula T_3M_2C (T = transition metal, M = simple metal of group IIB, III or IV of the periodic table, and C = carbon) are interstitial carbides where the parent-lattice consists of an ordered β-Mn-type structure, the carbon filling the octahedral voids in a surrounding of the transition element atoms. The same is true for the H-phase (T_2MC as described by Jeitschko, et al.[16]), the perovskite carbide of the Nowotny phases[17] (hex. D8C type). The main feature of these ternary carbides is the octahedral environment of the carbon atom (and occasionally the nitrogen atom) with respect to the transition metal atoms, while no bonding exists between simple metal atoms and carbon (nitrogen). Nowotny, et al.[18] have reported the following ternary carbides and nitrides which form in the β-Mn structure: V_3Zn_2N, V_3Ga_2N, Nb_3Al_2C, Nb_3Al_2N, Ta_3Al_2C, Mo_3Al_2C. Of these compounds Mo_3Al_2C and Nb_3Al_2N(T_c = 1.3°K[19]) have been found superconductive.*

Recently Kuz'ma, et al.[20,21] have reported a similar structure in the W-Re-C system. Their results show this compound, W_3Re_2C, is in equilibrium with a solid solution of Re and β-W_2C above 1500°C and with WRe_{2-3} (α-manganese structure) below 1500°C.

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* Nb_3Al_2C and Ta_3Al_2C samples have been tested in this laboratory and found normal to 4.2°K but the β-Mn structure could not be detected in any of these samples because of the intervening hexagonal structure, the H-phase.

A. Experimental

Samples of W_3Re_2C were prepared by hot-pressing the stoichiometric powder-mixtures in graphite dies at 2000°C. Some of these samples were then annealed in the temperature range of 2250°C to 2500°C in vacuum (10^{-5} torr) and gas quenched. The crystal structures of the samples were identified from x-ray diffractometer traces of both bulk and powdered samples. Photomicrographs clearly show a second phase (Fig. 2) and electron microprobe analysis indicates that the second phase contains an extremely low concentration of rhenium (Fig. 3). The results identify our samples as similar to those of Kuz'ma et al.[20,21] described in his paper as "'as cast' and annealed above 1500°C."

W_3Re_2C (β-Mn structure) was found superconducting at 7.4°K, the critical temperature decreasing with decreased carbon content (Table I). A sample converted almost entirely to β-W_2C (NaCl structure)(Fig. 4) by annealing in carbon at 2400°C showed no superconducting transition above 4.2°K. Magnetic field data on two of the samples are also included in Table I showing that this compound has a H_{c2}/T_c ratio of 6.9-7.4 or approximately one-half that observed for Mo_3Al_2C.

B. Discussion

Experimental and theoretical attempts to evolve concretely the criteria for superconductivity in elements, alloys and materials still persist. Some of the oldest and most useful criteria have been found in Matthias' rules.[3] These were developed empirically and then qualitatively shown by Pines[22] to be derivable on the basis of the now generally accepted microscopic theory of Bardeen, Cooper, and Schrieffer.[23] The primary empiricism of Matthias' rules is the prediction that alloys with average numbers of valence electrons per atom of 4.7 and 6.6 are the most favorable for high transition temperatures. The average number of valence electrons is taken directly from the periodic table (tabulated for the superconducting compounds with the β-Mn structure in column 1 of Table II).

In establishing the β-Mn structure as an electron compound having 7 electrons/atom, Bardos, et al.[11] have computed the electron concentration on the basis of electrons per transition metal atom (tabulated in column 2 of Table II). That this might not be a good basis is certainly shown in the case of Mo_3Al_2C with a T_c of 10°K and an e/a, on the above basis of 8.0. In looking at variations of T_c across the periodic table as Matthias did,[3] an e/a of 8.0 would be located at a minimum for superconducting properties and a T_c of 10.0 at this e/a value would be highly unlikely.

Another possibility for these filled and ordered β-Mn compounds is shown in column 3 of Table II where the interstitial atoms are considered to give up all of their electrons but only the atoms of the parent lattice are counted (i.e., electrons per parent lattice site). The only great change using this basis over that in column 1 where all atoms are

counted is shown by the compound W_3Re_2C where e/a has been increased from 6.0 to 6.4, which is much more favorable to superconductivity as shown by Fig. 5. Of course, in reality nothing can be determined by three examples but even these three samples (especially when looking at the compound W_3Re_2C) show that this possibility cannot be overlooked when considering interstitial compounds.*

One of the first serious attempts to predict superconducting properties from structural similarities has been made by Sadagapan and Gatos[28] in the case of superconductivity in transition metal carbides and nitrides. They consider the carbon-centered transition-atom octahedron, which is the common crystallographic characteristic of these materials, to be primarily responsible for superconductivity in these compounds. They classify these compounds into three categories on the basis of the Metal (T^I) to nonmetal (X) ratio (T^I/X): (1) $T^I/X = 1$; in this case each atom T^I is shared by six octahedra; phases with B1 structure such as TiC and NbC, (2) $T^I/X = 2$; in this case each T^I atom is shared by three octahedra; phases such as Mo_2C, H-phases, etc., (3) $T^I/X = 3$; here every T^I atom is shared by two octahedra phases such as β-Mn types ($T^I_3M_2X$), perovskite type (T_3^IMX) and the Nowotny phases. They conclude by reviewing the superconducting properties of a group of molybdenum carbides

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* A similar conclusion was reached for relatively dilute interstitial solid solutions of hydrogen, oxygen, and nitrogen in group V and VII transition metals by Ralls and Wulff.[26] They pointed out that the interstitial atoms may donate electrons to the metal, but the interstitial atom cores are not counted when valence-electron-to-atom ratio is determined. This is true because only the transition metal atoms have d-electron levels, which are most important for the superconducting properties of the transition metals,[27] and the d-band must be only slightly perturbed by the interstitial atom cores.

(Table III) that the higher the number of octahedra sharing the transition metals atoms, the higher the T_c value. Thus they predict from the behavior of the binary carbides or nitrides (B1-type structure) the superconductivity of a number of higher order compounds with crystallochemical similarities to this structure.

Applying their conclusions from the molybdenum carbides to a similar group of tungsten carbides the superconductivity of W_3Re_2C (β-Mn structure, $T^I/M = 3$) can be predicted since WC (cubic, B1) has been found superconducting at 10.0°K.[29] But, on the other hand, using the same argument, the compounds crystallizing in the ($T^I/M = 2$) H-phase as found by Nowotny et al.[16] should be even more favorable for superconductivity than the β-Mn structure ($T^I/M = 3$). This would especially be true of those compounds containing Nb-, Ta-, or Mo- atom octahedron, since the binary carbides of these three elements have relatively high critical temperatures. Several of these compounds have been tested[18] including two of these containing niobium, Nb_2InC and Nb_2SnC. No superconducting transitions above 1.1°K were observed for any H-phase tested and it was concluded that the H-phase structure itself is not favorable for superconductivity.[18]

IV. TWO-PHASE MICROSTRUCTURES

The superconductive properties of two-phase mixtures are of great interest in the field of superconductivity because most of the commercial superconductors in use today are necessarily two-phase mixtures due to their processing history. Early work on two-phase mixtures[30] demonstrates clearly that when a minority phase becomes superconducting, frequently the entire alloy sample appears superconducting to resistive measurements, having a T_c that is equal to or less than the T_c of that pure phase. The sample can also appear fully diamagnetic as well, as shown by Hudson[31] with some Ge-Sn alloys. In none of these early studies are photomicrographs of the structure available.

In more recent studies the question as to what transition temperature will be measured in a sample containing two superconducting phases with different transition temperatures has been shown by Merriam, et al.[4] to have several possible answers:

1. The entire sample may appear to become superconductive at the higher T_c.
2. The entire sample may appear to become superconductive at the lower T_c.
3. A partial transition may be observed at the higher T_c with the remainder of the specimen becoming superconductive at the lower T_c.
4. An entirely new transition temperature may be observed (intermediate between those of the two phases).

All four of these possibilities were observed in the mercury-indium system, depending on the physical distribution of the phases. Since the distribution of the phases is so critical to the properties, any study on multiple phase systems must include careful metallographic work.

A. The NbC-Nb_3Sn System

The theories of London,[32] Pippard,[33] and Ginzburg and Landan,[34] all predict the finite penetration of magnetic field into superconductors, and very large enhancement of critical fields when the dimension(s) of the superconductor becomes small compared to the characteristic penetration depth. The possibility, therefore, arises that very hard superconductors may be synthesized by suitable manipulation of the microstructure to achieve networks of thin superconducting filaments. Bean, et al.[35] have succeeded in the above by pressing mercury into porous Vycor glass; the critical field in this case was at least twenty times greater than the critical field of bulk mercury.

1. Experimental

Powders of Nb, Sn, NbC, and spectrographic C were hot-pressed in graphite dies at 2000°C for 10 min. at 7900 psi pressure in the proportions indicated in Table IV. X-ray analysis of all samples showed only an NaCl structure identified as NbC, a ≃ 4.5Å.

Metallographic examination of samples of $Nb_{0.50}Sn_{0.33}C_{0.17}$ of nominal composition showed very dense hard NbC (Fig. 6) and micro-probe results on these samples showed that the Sn was concentrated in the grain boundaries (Fig. 7). All other compositions used yielded very porous incompletely sintered compacts as shown in Figs. 8 through 10.

2. Discussion

Sintering of pure refractory hard metals (carbides, nitrides, borides, and silicides) is not fully understood. Most of the recently developed hard metal-base refractories are cemented, that is, metal-bonded materials. In these systems, sintering takes place in the presence of a liquid phase which in most cases is represented by a eutectic composition. The only practical way of consolidating hard-metal powders in the absence of binders appear at present to be hot-pressing procedures. But the common industrial practice is to fabricate carbides mixed with up to 14 wt % of a metallic binder (cobalt or nickel) by hot-pressing in graphite dies.

The hot-pressing characteristics of commercial carbide powders are greatly influenced by metallic impurities. In particular L. Ramquist[36] has noted that those impurities that concentrate principally at the grain boundaries cause rapid grain growth by formation of a micro-eutectic or solid solution at the grain boundaries which facilitates material transport during hot-pressing. He uses the WC + Co system to illustrate the influence of a liquid phase on hot-pressing. The micrograph of WC + 0.25 wt % Co hot-pressed at 2100°C for 8 min. at 400 kG/cm^2 pressure has a micro-structure very similar to that exhibited by the $Nb_{0.50}Sn_{0.33}C_{0.17}$ samples in this investigation. Thus the Sn or excess Nb + Sn might be acting as a "binder" during hot-pressing.

The superconducting critical temperature of the $Nb_{0.50}Sn_{0.33}C_{0.17}$ samples (T_c = 17.2-16.0°K) suggests that this grain boundary phase is actually Nb_3Sn (T_c = 18.1°K).*

* The slight lowering and broadening of the Nb_3Sn transition in the $Nb_{0.50}Sn_{0.33}C_{0.17}$ samples from that of pure Nb_3Sn can probably be associated with the size of the superconducting phase similar to results of H.E. Cline et al.[37] on Nb wires in a Cu matrix.

This is the only superconducting transition observed in these samples and therefore it must be assumed that the "mesh" of Nb_3Sn is able to completely shield the bulk NbC (T_c = 11.1°K). The magnetic field data are also consistent with the filamentary nature of the Nb_3Sn phase. The critical current density J_c (even low fields) is very small, but at low current densities (50-100 amp/cm^2) the critical field H_r is higher than the highest field obtainable in this study (~200 kG). This is consistent with the results obtained by other investigators[38,38] on samples with similar microstructure.

The samples which have been prepared with a 1:1 ratio of Nb to C or commercial NbC powder all exhibited low T_c's (Table IV)(i.e., that for NbC)* and very porous microstructures (Figs. 8 through 10). The micrographs show a decrease in porosity when Nb_3Sn is used as a binder instead of Sn in pressing the commercial NbC (Figs. 8 and 9). It can also be seen that the porosity is reduced even further if Nb powder and spectrographic carbon (1:1 ratio) are used instead of prepared NbC with the binder metal (Fig. 10). A complete study of the hot-pressing characteristics of this system are now in progress in this laboratory.

* The broad transitions and range of transition temperatures observed in these samples is probably due to the strong dependence of T_c on composition in the carbides.

B. Ta-Zr System

At elevated temperatures alloys of the transition elements from group 4 to 6 in the periodic table exhibit wide ranges of mutual solubility in the bcc structure. Except for compositions that are high in a group 4 element, the bcc structure can be retained at room temperature by quenching and several systematic studies of the influence of composition on superconductivity in bcc alloys have been reported.[25,39] Specifically Hulm and Blaugher[25] in the first extensive investigation of binary alloys of transition metals observed two transition temperature maxima with electron-to-atom ratios of approximately 4.7 and 6.4, respectively, for alloys formed between neighboring elements in a given row of the periodic table.

More recent work on commercially interesting solid solution alloys such as Nb-Zr[25,40-45] and Nb-Ti[25,45,46] have shown that the superconducting transition temperature and the resistive critical magnetic field (Hr) are structure-sensitive. Studies of Ta-Ti alloys[45,47-50] show they remain superconducting at fields comparable to Nb-Ti alloys.[45,47,50] But no superconductive information is available on the Ta-Zr system.

The Ta-Zr system exhibits a minimum melting point type phase diagram (Fig. 11) that has the same form as the commercially interesting Nb-Zr system. Alloys in the range 6.5-9.55 at. pct. Zr undergo a separation into two body-centered cubic phases at temperatures from 1775°C to 785°C. At 785°C the monotectoid reaction should produce primary Zr and Ta solid solutions, where the latter reaction is very sluggish due to relatively low diffusivities in Ta. Many of the superconductive properties of the Nb-Zr alloys are related to phase separation. The present study of Ta-Zr alloys was undertaken to examine the influence

of microstructure, as controlled by composition and heat treatment, on the superconducting transition temperature, T_c.

1. Experimental

Alloys were prepared by melting tantalum and zirconium (iodide crystal bar) mixtures in an arc furnace on a water-cooled copper hearth using a tungsten electrode. Melting was accomplished in a purified, gettered argon atmosphere at a pressure of approximately 400 Torr. Each sample was turned and remelted seven times to assure complete mixing of tantalum and zirconium. To produce single phase specimens, alloys were heat-treated in vacuum (10^{-6} Torr) for 18 hours at 1800°C and quenched with distilled water atomized into a high velocity helium. The subsequent aging treatment of Ta-20 pct. Zr and Ta-50 pct. Zr alloys was done in vacuum (10^{-6} Torr) for 24 hours at 1500°C and quenched as above. The phases present in the single phase and aged alloys were identified by optical metallography and electron beam microprobe analysis.

2. Discussion

The superconducting transition temperatures for alloys quenched from 1800°C (Fig. 12) exhibits a maximum of 7.5°K near 15 at. pct. Zr (4.85 valence electrons per atom). The maximum T_c at 4.85 valence electrons per atom is in accord with De Sorbo's correlation which utilizes an effective electron-to-atom ratio.[52]

The superconducting transition temperatures of Ta-20 pct. Zr and Ta-50 pct. Zr are shown in Table V for aged specimens quenched from 1800°C and for those aged at 1500°C for 24 hrs. The microstructure of the 20 pct. Zr alloy consists of a fine scale precipitate which is within the limit of resolution of the optical microscope but on too fine a scale for electron beam microprobe analysis. From the phase diagram (Fig. 11) it is seen that, at equilibrium, alloys aged at this temperature should be composed of two bcc phases of approximately 8 and 77 at. pct. Zr, respectively. The superconducting transition in this sample shows a high degree of broadening, occurring over a 1.0°K temperature interval (6.2° to 7.3°K). This transition is lower than that observed for single phase samples of 20 at. pct. Zr, but is not as low as would be observed for a single phase sample containing 77 at. pct. Zr (i.e., 5.5°K). Thus this represents an intermediate transition temperature where the broadening can be related to the scale of the precipitated particles. The same type of transition broadening has been observed in Zr-Rh alloys with a similar type of microstructure.[53]

The microstructure of the 50 pct. Zr alloy is characterized by much larger precipitate particles. Microprobe results show the zirconium content of the particles to be 8.5 at. pct. and that of the matrix to

be 72.7 at. pct. The 8.5 pct. Zr phase is also present in the grain boundaries. This sample exhibits a very sharp superconducting transition (0.1°K width) at 7.3°K. This transition temperature is almost a full degree higher than that observed for single phase samples of 50 at. pct. Zr and is characteristic of the 8.5 pct. Zr phase. With longer aging times at 1500°C the superconducting transition of the Ta-20 pct. Zr alloy should also reach 7.3°K as a limiting value. This variation with aging time was observed by Hehemann and Zegler[44] on Nb-Zr alloys of two different compositions.

V. SUMMARY

Metallurgists have relied heavily on several empirical guides to find new superconductors and improve the preperties of known superconductors. Two of these guides which have made possible the great advances in the technology of commercial superconductivity have been (1) studies based on the crystal structures of known superconductors and (2) studies of binary solid solutions of known superconductors. Use of these two empirical guides has led to the discovery of scores of new superconductors[54] and recently, to the discovery of one superconductor with a transition temperature of 20°K (found for a solid solution alloy between Nb_3Al and Nb_3Ge[55]). With the advent of high field superconductivity, correlations of microstructure to the superconducting properties of known high field superconductors have also become useful guides in improving superconducting properties. Using these empirical guides, this investigation has led to (1) the discovery of a new superconductor (W_3Re_2C, β-Mn structure, at 7.4°K); (2) the formation of a synthetic high-field superconductor with a filamentary microstructure (Nb_3Sn in a NbC matrix, critical field higher than 200 kG at low current densities); (3) the observation of a maximum in the superconducting transition temperature of Ta-Zr alloys (max. 7.5°K at 15 at. pct. Zr); and (4) the increase of T_c by heat treating Ta-50 pct. Zr alloys within the miscibility gap of the Ta-Zr system (6.5°K for samples quenched from 1800°C and 7.3°K for samples heat treated at 1500°C for 24 hours).

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APPENDIX

Materials Used:

Carbon, Union Carbide Corporation, New York, Spectroscopic Powder, Grade SP-2.

Niobium, Kawecki Chemical Co., Boyntown, Pa., -325 mesh powder, 99.9% pure.

NbC, Fansteel Metallurgical Corporation, North Chicago, Illinois, -325 mesh powder, 99.9% pure.

Rhenium, Chase Brass and Copper Co., Inc., Waterburg, Conn., -325 mesh powder, 99.99% pure.

Tantalum, Fansteel Metallurgical Corp., North Chicago, Illinois, rod 99.99% pure.

Tin, Cominco Electronic Materials, Spokane, Washington, -200 mesh powder, 99.9% pure.

Zirconium, Nuclear Materials and Equipment Corp., Apollo, Pa., iodide crystal bar, 99.95% pure.

TABLE I

X- Ray Results

Heat Treatment	Major Phase	Second Phase	T_c(°K)	H_{c2}(kG)
As Cast	β-Mn, a = 6.86	FCC, a ≃ 4.4*	7.3-7.5	———
annealed in vac., 2250°C (20 mins) 2400°C (30 mins), quenched	β-Mn, a = 6.86	FCC, a = 4.38	7.1-7.3	53.5(4.2°K)
annealed in vac., 2500°C (20 mins), quenched	β-Mn, a = 6.86	FCC, a = 4.38	7.0-7.2	———
annealed in vac., 2400°C (1 hr.), quenched	β-Mn, a = 6.86	FCC, a = 4.38	6.6-6.9	46.5(4.2°K)
annealed in Carbon,	FCC, a = 4.35	β-Mn, a = 6.68*	normal to 4.2°K	———

* Diffractometer results showing the transformation in crystal structure from "as cast" to "annealed in carbon" are presented in Fig. 4.

TABLE II

Electron Concentration

Compound	T_c(°K)	Valence electron / atom	Valence electron / T metal atom	Valence electron / parent lattice atoms
Mo_3Al_2C	10.0[10]	4.67	8.0	4.8
Nb_3Al_2N	1.3[11]	4.33	7.0	4.2
W_3Re_2C	7.4	6.0	6.4	6.4

TABLE III[17]

Number of Octahedra Sharing the Transition Metal Atoms

Composition	Crystal Structure	Mo Atoms	T_c(°K)
$Mo_{4.8}Si_3C_{0.6}$	hexagonal, $D8_8$	2	7.6
Mo_3Al_2C	cubic, β-Mn	2	10.0
Mo_2C	orthorhombic	3	12.2
Mo_2C_{1-x}(a)	orthorhombic	3	10.8
Mo_2C_{1-x}(b)	orthorhombic	3	8.1
α-MoC_{1-x}	cubic, B1	6	13.5
$Mo_{0.5}Hf_{0.5}C_{0.75}$	cubic, B1	6	14.2

(a) Prepared from 72μ particle size powder.

(b) Prepared from 44μ particle size powder.

TABLE IV

Starting Composition	X-ray Results	T_c(°K)
$Nb_{0.50}Sn_{0.33}C_{0.17}$	NbC (NaCl structure, a ≃ 4.5Å)	17.2-16.0
$Nb_{0.30}Sn_{0.40}C_{0.30}$ (i.e., NbC + 60 wt% Sn)	NbC	11.2-10.9
$(NbC)_{0.95}Sn_{0.05}$ (i.e., NbC + 10 wt% Sn)	NbC	11.2-9.0
$(NbC)_{0.90}Sn_{0.10}$ (i.e., NbC + 20 wt% Sn)	NbC	10.7-10.2
$(NbC)_{0.92}(Nb_3Sn)_{0.08}$ (i.e., NbC + 10 wt% Nb_3Sn)	NbC	11.35-9.6

TABLE V

Composition	Transition Temperature (°K) Single Phase (1800°C)	Two Phase (1500°C)
Ta-20 pct. Zr	7.5	6.2 - 7.3
Ta-50 pct. Zr	6.5	7.3

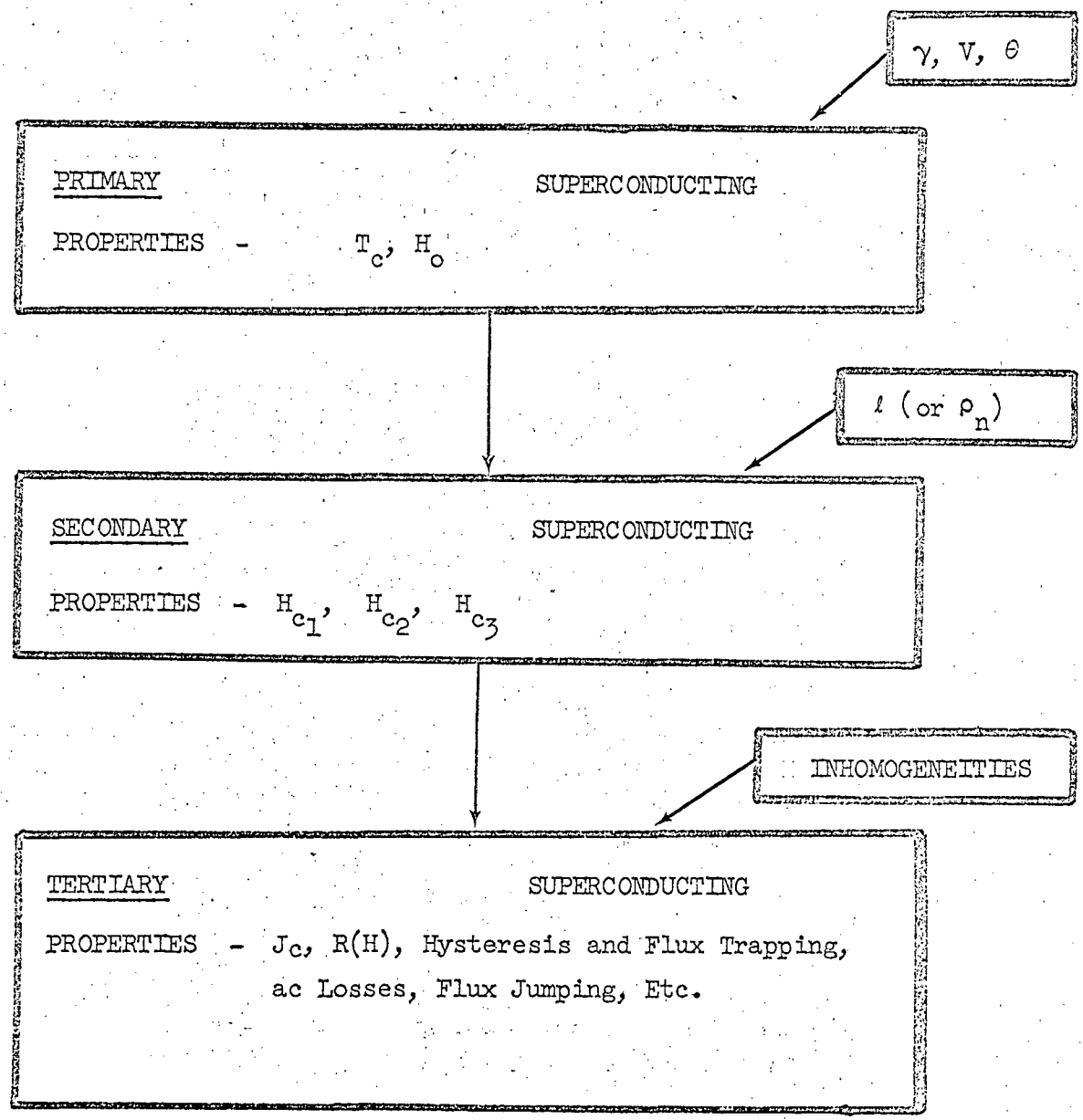
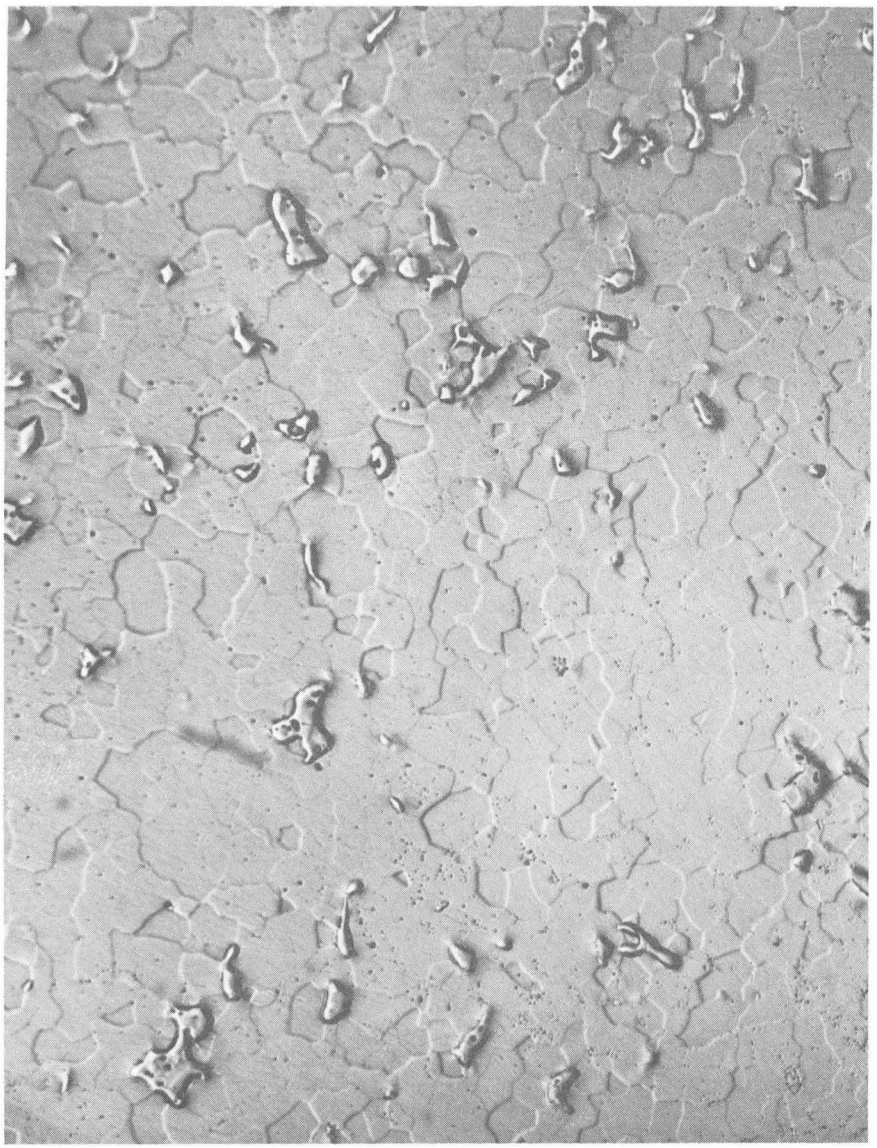
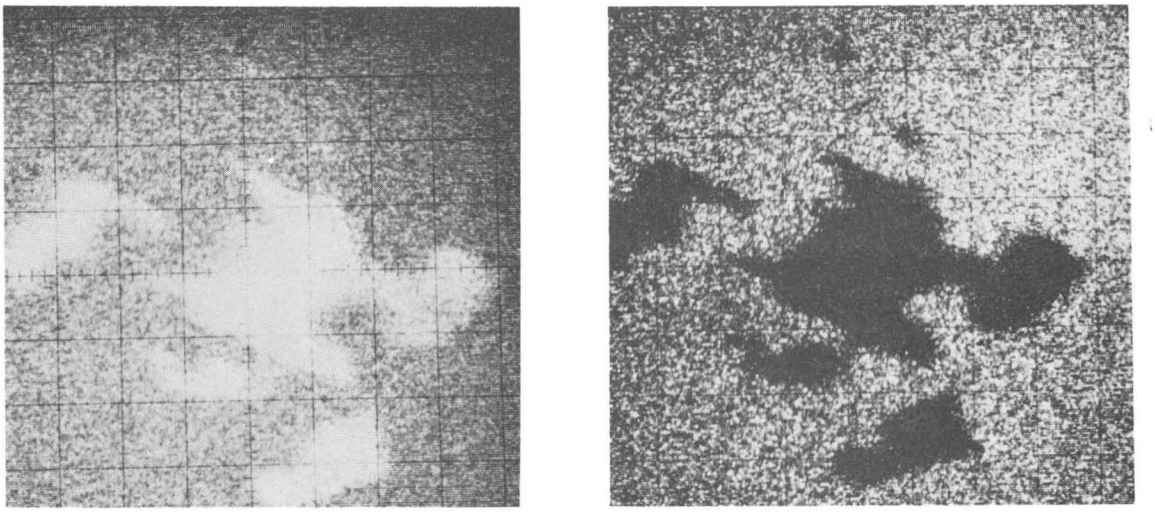


Fig. 1 Schematic representation of the relation between primary, secondary, and tertiary superconducting properties. Primary properties are relatively structure-insensitive, secondary properties are sensitive to mean free path ℓ, and tertiary properties are sensitive to inhomogeneities.



ZN-5817

Fig. 2 Microstructure of hot-pressed W_3Re_2C (β-Mn structure) plus second phase [250×]



ZN-5816

Fig. 3 Electron microprobe display patterns of rhenium characteristic x-radiation (left) and of tungsten characteristic x-radiation (right) for specimens shown in Fig. 2 [about 1000×].

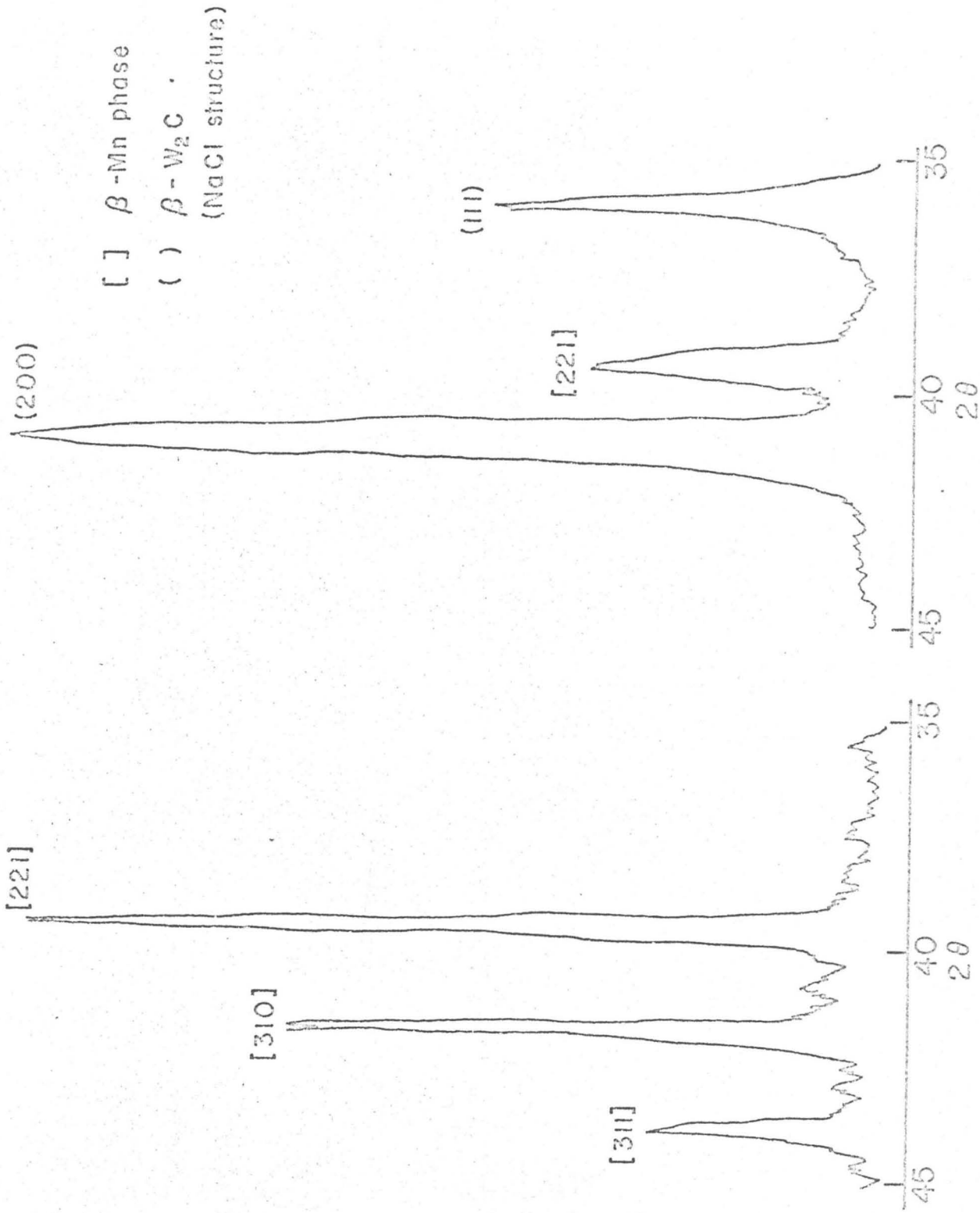


Fig. 4 Diffractometer results showing the transformation in crystal structure from the β-Mn structure (W_3Re_2C, a_o = 6.86 Å) to the NaCl structure (β-W_2C, a = 9.35 Å).

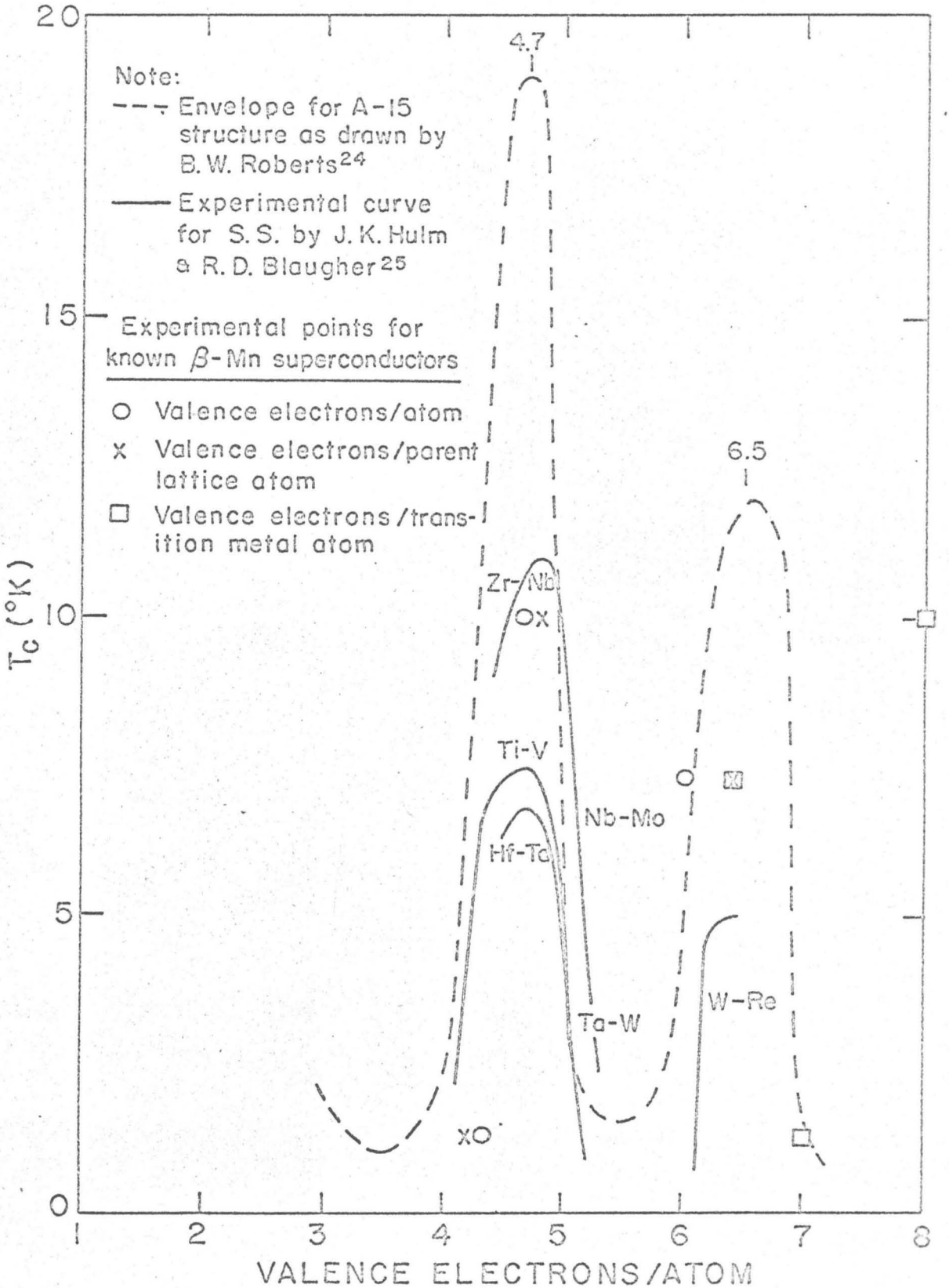
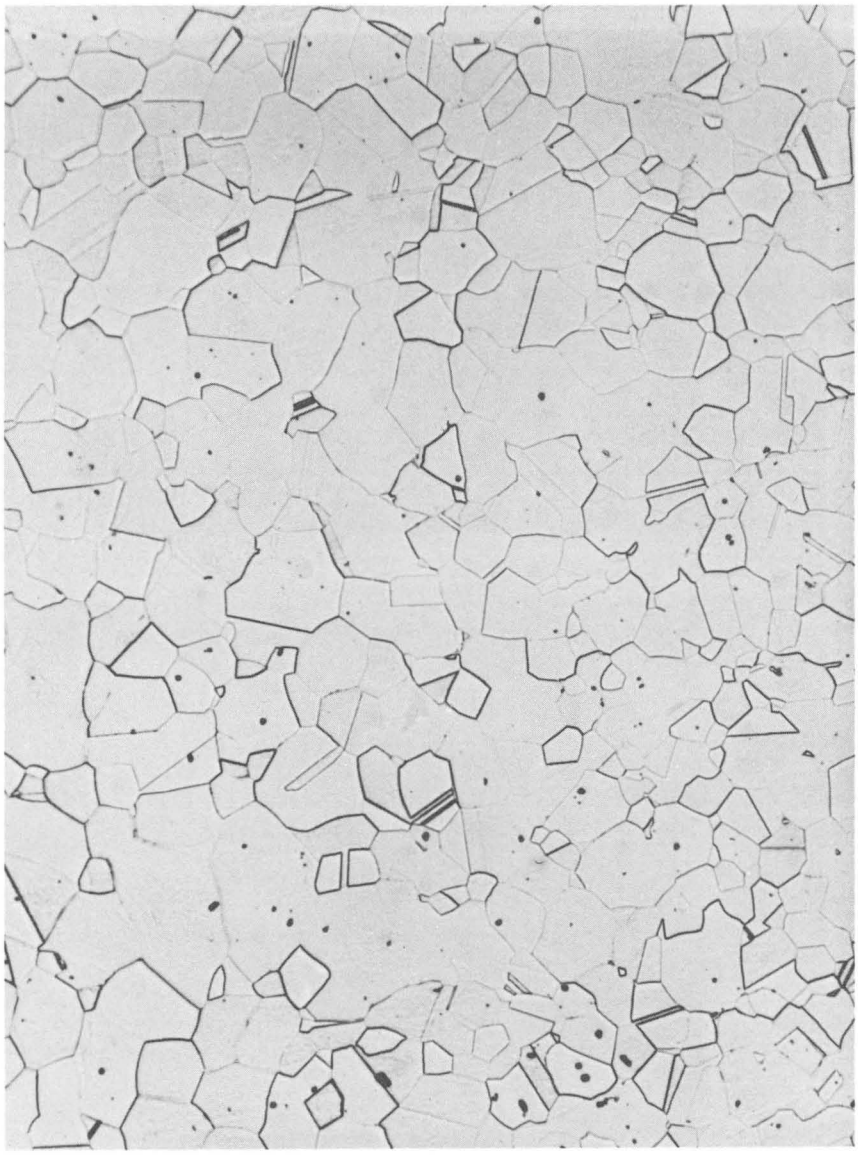
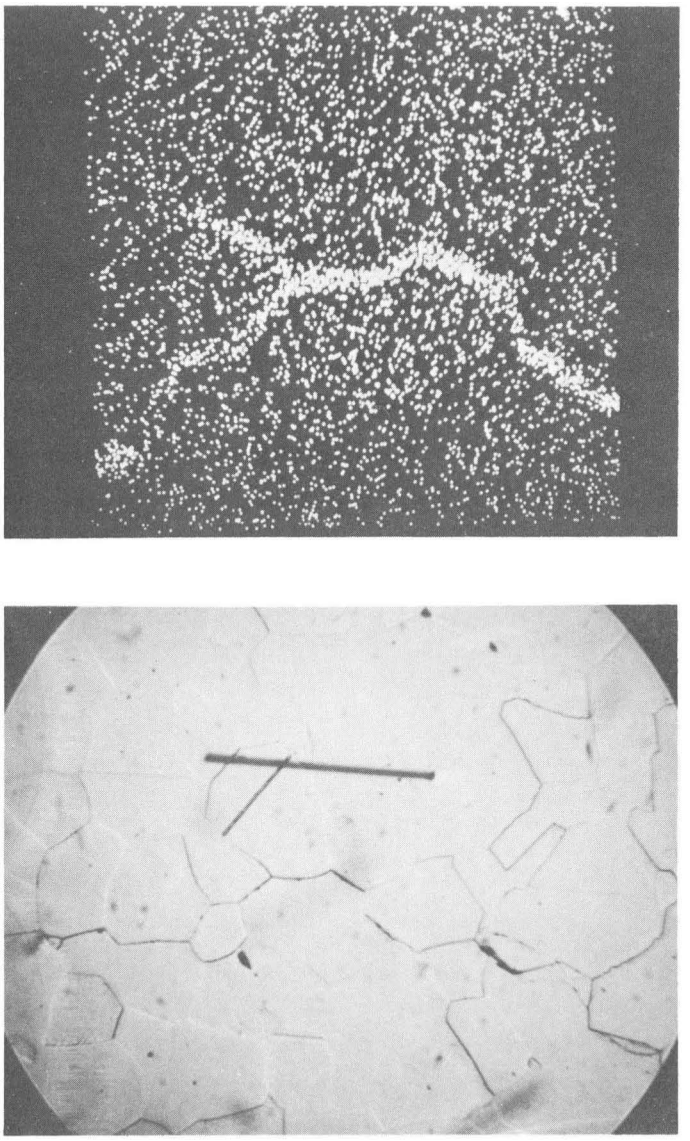


Fig. 5. Critical temperature versus valence electron per atom ratio for β-Mn type compounds compared to experimental curves for bcc solid solution alloys (Hulm and Blaugher[25]) and for β-W type compounds (Roberts[24]).



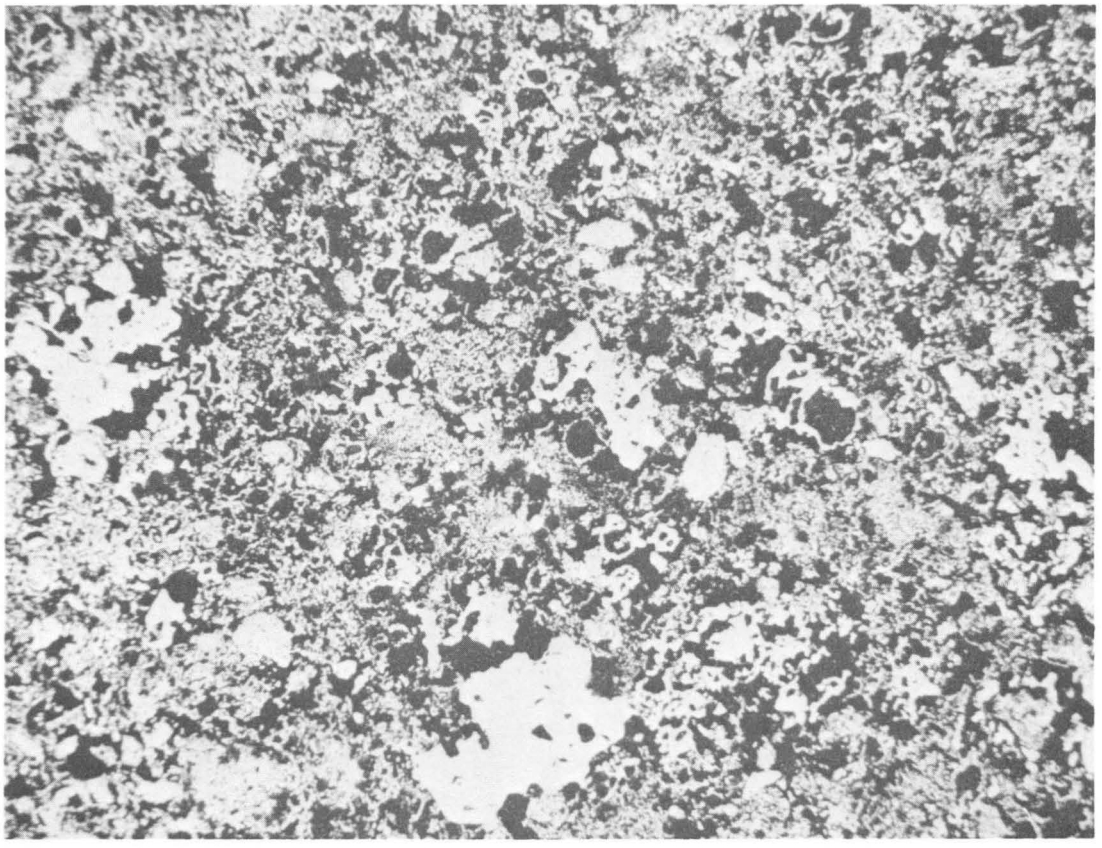
XBB 675-2691

Fig. 6 Microstructures of hot-pressed $Nb_{.50}Sn_{.33}C_{.17}$ [500×].



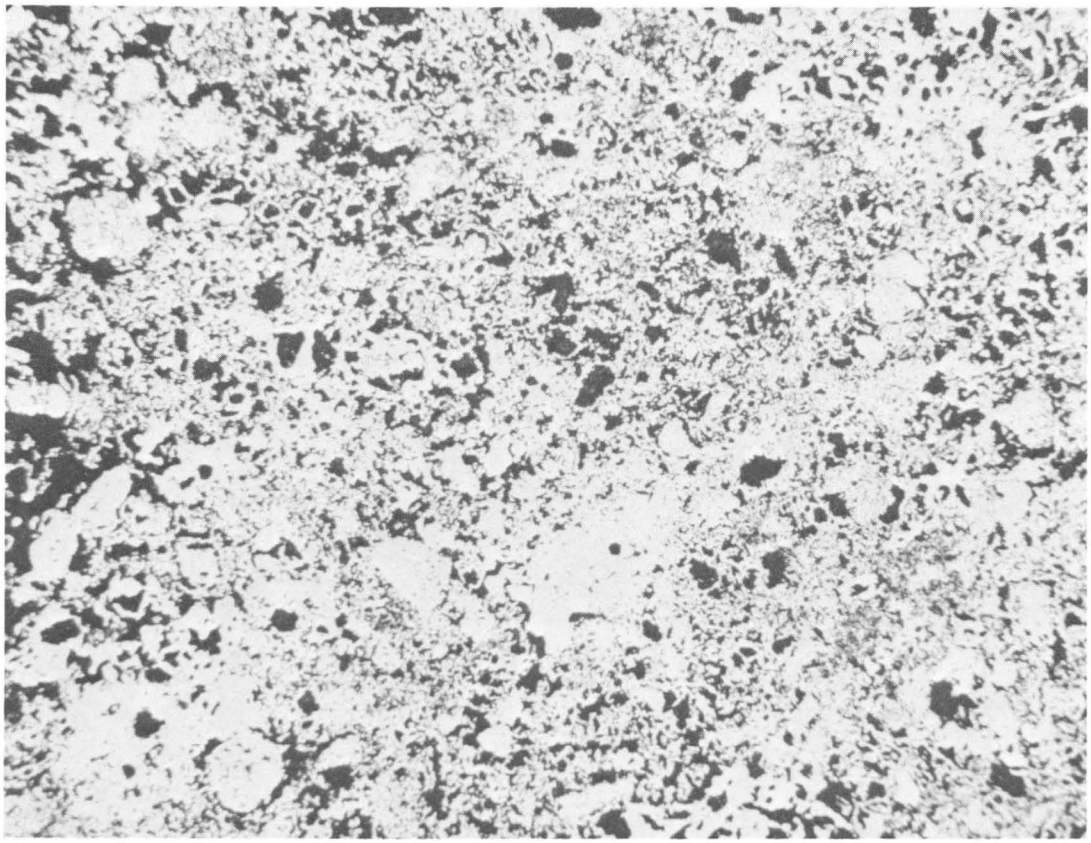
XBB 675-2711

Fig. 7 Optical micrograph of hot-pressed $Nb_{.50}Sn_{.33}C_{.77}$ (about 250×) and electron microprobe display pattern of tin characteristic. X-radiation of grain boundary area (about 1000×).



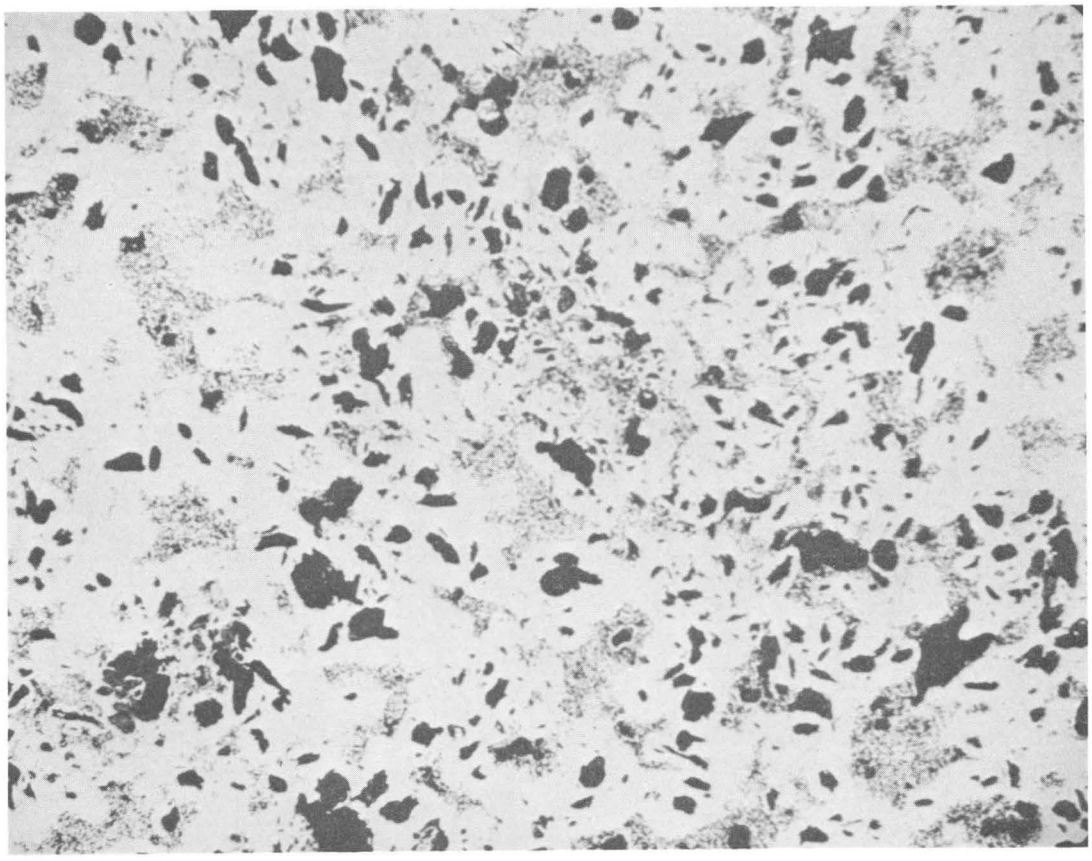
XBB 675-2689

Fig. 8 Microstructure of hot-pressed NbC + 10 wt.% Sn (63×).



XBB 675-2690

Fig. 9 Microstructure of hot-pressed NbC + 10 wt.% Nb_3Sn (63×).



XBB 675-2688

Fig. 10 Microstructure of hot-pressed NbC + approximately 60 wt.% Sn (63X).

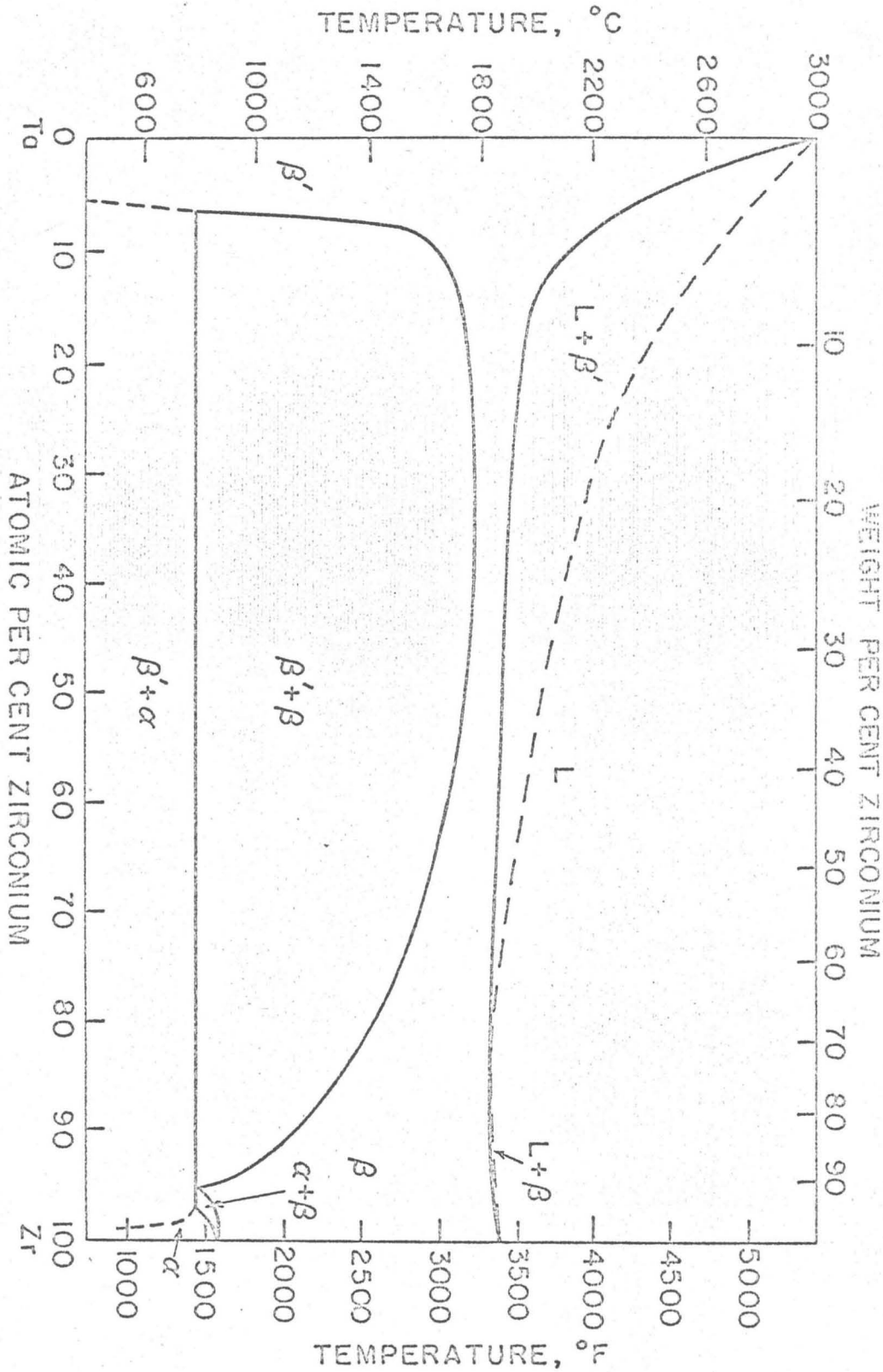


Fig. 11 Tantalum-zirconium phase diagram (after Pease and Brophy[51]).

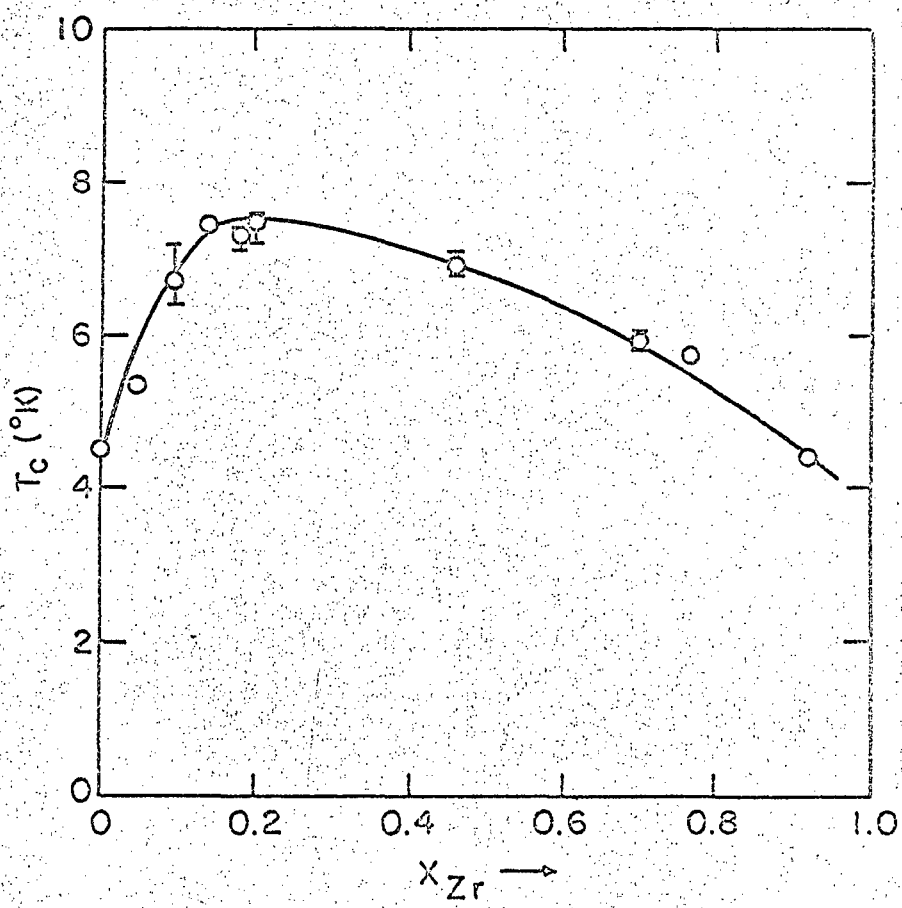


Fig. 12 Superconducting transition temperature of tantalum-zirconium alloys.

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