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SUPERCONDUCTIVITY IN SOLID SOLUTIONS OF
TRANSITION METAL CARBIDES

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OF TRANSITION METAL CARBIDES

Molly Wells

(M.S. Thesis)

June 1964

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SUPERCONDUCTIVITY IN SOLID SOLUTIONS
OF TRANSITION METAL CARBIDES

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June 10, 1964

ABSTRACT

In crystal structures favorable to superconductivity in intermetallic compounds successful empirical studies have been made relating lattice parameter, electrons per atom, and electrons per unit volume to the superconducting transition temperature. The system of solid solutions of TaC and NbC was studied to ascertain whether similar empirical correlations existed for the cubic NaCl structure. Critical temperature showed a maximum higher than the critical temperature of either pure carbide. In this system, electrons per atom remained constant, while lattice parameters varied linearly. The results of this study show that the parameters successfully applied to intermetallic compounds are insufficient to describe superconductivity in the cubic NaCl system.

I. INTRODUCTION

A. History

In 1911 Kammerlingh Onnes was studying electrical properties of materials at low temperatures. Liquid helium, which he had learned to produce three years earlier had opened the way to research in the temperature range from 1 to 14°K. While taking a low temperature resistance measurement of mercury, he observed a total disappearance of resistance at 4.2°K.

Resistivity of metals was known to decrease as the material was cooled. Onnes' intention was to discover whether this trend would continue to absolute zero, or whether on further cooling resistivity would remain constant or even increase again.

It was reasonable to expect that if electrical resistance was primarily due to scattering of electrons by the lattice, resistance would approach zero smoothly as the material was cooled. As the lattice energy gradually decreased, lattice vibrations would approach zero, and the resultant scattering of electrons would disappear.

If low temperature resistivity was due to impurity centers and crystal defects, the resistance would be expected to approach some value greater than zero. An increase in resistivity with lowering temperature would occur if the conduction electrons condensed on the metal atoms and ceased conducting electricity.

Onnes, working with platinum, discovered that resistivity became constant as the temperature was lowered. He concluded that resistance was due to impurities. His research continued on mercury, a substance

he felt could be purified to a higher degree than platinum. At 4.2°K , electrical resistance totally disappeared in a temperature interval less than $.05^{\circ}\text{K}$.

Prior to that time, in 1910, Onnes had observed the resistance of very pure gold wires to be zero, to the accuracy of his measurements, in the temperature range of liquid helium. Since that time, however, gold has been found to be non-superconducting.

From this relatively simple beginning the field of superconductivity has become increasingly complex. The temperature of the superconductive transition was discovered to be a function of an applied magnetic field. Fields of sufficient strength could completely suppress the superconductive transition. The critical temperature was also found to be related to various physical or chemical properties of the materials.

Many phenomenological theories have been proposed to describe the occurrence of superconductivity on the basis of thermodynamics and electron theory. Somewhat less theoretical studies have attempted to correlate transition temperature with physical and crystal-chemical parameters.

B. The Meissner Effect

For twenty years, researchers assumed that superconductivity was synonymous with perfect conductivity. Unfortunately, perfect conductivity implied that the transition was irreversible or dependent on the path of the transition.

If a normal conductor were placed in a magnetic field, cooled below its transition temperature, and the magnetic field removed, then a current would be set up on the surface of the superconductor which would trap the

magnetic flux (Fig. 1)¹. On the other hand, if the conductor was cooled below its transition temperature before the magnetic field was applied, the application of the field would induce surface currents which would disappear when the field was removed (Fig. 2)¹. Whether a magnetic field was applied before or after the superconductive transition seemed to determine the final state.

This apparent difficulty was resolved with the discovery of the Meissner effect. Ideal superconductors, regardless of the path of the transition exclude magnetic flux. Thus, an ideal superconductor does possess zero electrical resistance and is also a perfect diamagnet with diamagnetic susceptibility of $-\frac{1}{4}\pi$. The Meissner effect is characterized by total flux exclusion up to a magnetic field H_c . Above this critical field, there is no superconductive transition. The critical field is dependent on temperature according to the formula:

$$H_c = H_0 \left[1 - \left(\frac{T}{T_c} \right)^2 \right]$$

where H_0 is the critical field strength at absolute zero.

C. Type II Superconductivity

Most alloys, as opposed to pure elements, exhibit only a partial Meissner effect. These materials, the "hard superconductors" or type II superconductors have two critical field strengths. One of them, H_{c2} , is the field above which no superconductivity is observed, while H_{c1} is the field below which a total Meissner effect is observed. The behavior of the type II superconductors is best described by the Mendelssohn sponge model.² Type II superconductors do not exhibit a new phenomenon, but

are described as a mesh of superconducting filaments within a normal matrix. These filaments have higher threshold values than the remainder of the material. As the field varies, the fraction of the sample participating in superconductivity also changes. Of course, resistance disappears as soon as any fraction of the sample becomes superconducting, since any remaining normal regions are short circuited by the superconducting ones.

D. Penetration Depth and Coherence Length

The phenomenon of flux exclusion is characterized by a certain penetration depth of the external magnetic field. There is no discontinuous change from the applied field to the zero magnetization within the sample. London modified Maxwell's equations to obtain a relation

$$H(x) = H_0 e^{-x/\lambda}$$

where x is the distance from the surface, λ is the penetration depth, and H_0 is the applied magnetic field.

The exclusion of flux from a volume of superconducting phase requires an energy $\frac{H^2}{8\pi}$. Because the flux penetrates the surface to a depth λ , the energy of flux expulsion is changed by an amount $-\frac{\lambda H^2}{8\pi}$ per area of interface. This lowering of energy on creation of surface would seem to imply a spontaneous breaking up of the superconductor into alternating normal and superconducting regions. Because this does not happen in an ideal superconductor, it was hypothesized that there must be an interfacial energy term that normally outweighs $\frac{\lambda H^2}{8\pi}$.

The total surface energy may be written

$$\alpha_{ns} = \frac{H^2}{8\pi} (\xi - \lambda)$$

where ξ is the coherence length, the distance necessary for the transition from a normal to a superconducting phase. In an ideal superconductor, the coherence length is on the order of $10^4 \text{ \AA}$ and the penetration depth is approximately $100 \text{ \AA}$. The surface energy is positive, and there is no tendency to break up into small superconducting regions.

In hard superconductors the sponge structure, or alternating normal and superconducting regions, results from a negative surface energy. The coherence length can be decreased by impurities, alloying elements, or crystal imperfections because these defects scatter electrons and shorten the distance over which a change in electronic configuration can take place. These defects also serve to trap magnetic flux and result in much higher critical fields than those found in ideal superconductors.

E. Thermodynamic Treatment of Superconductivity

The thermodynamics of the superconducting transition was treated independently by several different groups. After the discovery of the Meissner effect, Gorter and Casimir³ were able to develop an analysis of the transition in a treatment analogous to other phase transitions.

The Gibbs free energy per unit volume of an ideal superconductor in a magnetic field is greater than the energy of the same conductor in zero field by an amount $\frac{H^2}{8\pi}$, the energy of the excluded flux lines.

$$G_s(H) = G_s(0) + \frac{H^2}{8\pi}$$

Because of the negligible susceptibility of a sample in a normal state, the free energy of a normal conductor in a magnetic field is approximately equal to that in zero field.

$$G_n(H) = G_n(0)$$

At the critical field, the phase transition takes place.

$$G_n(H_c) = G_s(H_c)$$

$$G_n(0) - G_s(0) = \frac{H_c^2}{8\pi}$$

The entropy is given by the equation

$$S = - \frac{\partial G}{\partial T}$$

$$S_n(0) - S_s(0) = - \frac{H_c}{4\pi} \left(\frac{dH_c}{dT} \right)$$

At the transition temperature the critical field is zero, and at absolute zero the first derivative of the critical field is zero. Between those two temperatures, the critical field is positive and its first derivative is negative. Therefore, the entropy of the normal phase is greater than the entropy of the superconducting phase in the temperature range between zero and the transition temperature. The entropies of the two phases are equal at zero and at the transition temperature.

The latent heat of the transition

$$Q = T(S_n - S_s)$$

is zero when the phase change takes place in no applied magnetic field. In the presence of a magnetic field, the latent heat is positive. This

feature suggested the possibility of cooling by adiabatic magnetization.

Further differentiation of the entropy equation and multiplication by T gives the result

$$C_s - C_n = \frac{T}{4\pi} \left(H_c \frac{d^2 H_c}{dT^2} + \left(\frac{dH_c}{dT} \right)^2 \right).$$

At the critical temperature, the specific heat of the superconducting phase is greater than that of the normal phase. A discontinuity in specific heat is predicted at the critical temperature. The superconducting transition is, therefore, a second order transition (Fig. 3)⁴.

The specific heats of the normal and superconducting phases can be considered a sum of contributions from the lattice and from the electrons. The first term is proportional to $(\frac{T}{\theta})^3$, where θ is the Debye temperature, and the second term is γT , where γ is the Sommerfeld constant, proportional to the density of electronic states at the Fermi surface. From specific heat experiments carried out at fields greater than the critical field, γ of the normal phase can be determined. If the contributions from the lattice are assumed to be equal in both phases, the specific heat in the superconducting phase can be calculated.

F. The BCS Theory

The electronic specific heat becomes important in the microscopic theory of superconductivity. Bardeen, Cooper, and Schrieffer⁵ arrived at an explanation which satisfactorily explains the phenomenon of superconductivity and is in accord with experimentally observed results.

For instance it had been observed that superconducting isotopes showed critical temperatures related by the equation

$$T_c \sim M^{\frac{1}{2}}$$

where M is the mass of the isotope. Transition temperatures had also been shown to be dependent on the frequency of an applied magnetic field. No superconductivity was observed at frequencies higher than 10^{13} sec^{-1} . It was concluded that at high frequencies, electrons which had condensed into a superconducting state were excited into a normal state. The energy gap is on the order of kT_c . The energy difference between normal and superconducting states, given by $\frac{H_c^2}{8\pi}$ is on the order of 10^{-8} e.v. The extreme smallness of this gap is obvious when it is compared with the energy of the Fermi surface, typically 10-20 e.v.

The BCS theory satisfactorily incorporates the experimental results. This theory suggests the formation of Cooper pairs, electrons of opposite spins and momenta at the Fermi surface coupled by exchange of a virtual phonon. The condensation of the electrons into a lower energy state results in the superconductive transition.

The important parameters in the BCS theory are the density of states at the Fermi surface, $N(0)$, an average phonon frequency, W_q , and an interaction parameter, V , which is a measure of the very weak attraction between the paired electrons. The critical temperature is given by the equation

$$T_c = \left(\frac{1}{k}\right) (1.14) W_q \exp \left[-\frac{1}{N(0)V}\right]$$

The limitation of this theory is that while it gives an explanation of superconductors of the first type, it does not give a formula for the production of a superconductor of high critical temperature or high field

characteristics. Clearly, since it is technologically easier to work at higher temperatures, materials having high T_c and H_c are more likely to be of practical use.

G. Empirical Relations

Many empirical rules have been found to describe the best crystal chemical properties for a high transition temperature. Superconducting elements are characterized by small atomic volumes.⁶ Favorable conditions also seem to be present when the number of valence electrons per atom is 3, 5 or 7.⁷ Correlations exist between electronic specific heat and T_c , since in alloys of variable composition these two parameters often have maxima at the same composition.

Pines⁸ attempted to relate these empirical formulas to the BCS theory and was partially successful. At least there is a periodic variation in $N(0)$ as a function of the number of valence electrons per atom, which gives a qualitative agreement with the favorable numbers of 3, 5 or 7 valence electrons.

Certain crystal structures are more favorable to superconductivity than others. Among the best is the Al₃ structure with compounds having formulas AB_3 . The lattice consists of a body centered cubic lattice of A atoms, with the B atoms forming mutually orthogonal, non-intersecting chains on the cube faces (Fig. 4)⁹. This class of compounds includes the highest critical temperatures known (Nb_3Sn , $T_c = 18.5$; V_3Si , $T_c = 17.0$).

For these compounds, the maximum mean atomic volume implies the highest critical temperature, with the exception of V_3Si and its modifications (Fig. 5).⁹ Other very striking correlations appear between

valence electrons per atom and electrons per unit volume (Figs. 6, 7).⁹

H. Superconducting Carbides

Another class of compound with a favorable crystal structure is the interstitial carbides and nitrides of the transition metals. These compounds have the NaCl structure, a face centered cubic lattice of metal atoms with carbon atoms in interstitial positions. Many of these compounds form continuous, often ideal, solid solutions with each other.

This study was undertaken to test the system of TaC-NbC. Both of these carbides are superconductors. Because the metals are members of the same column, they are electronically similar and are almost the same size. These characteristics minimized any effects from variation in electrons per atom or electrons per unit volume.

One of the serious problems involved in work with these carbides is that of stoichiometry. It has been suggested that the energy of formation of a carbon vacancy is lower than that for formation of a metal vacancy. Therefore, as the temperature is increased, the equilibrium number of carbon vacancies is considerably greater than the number of metal vacancies. At the lower temperatures where the numbers of carbon and metal vacancies are more nearly equal, the kinetics of the reaction are too slow to facilitate formation of the carbide.

Critical temperature has been shown to be highly dependent on stoichiometry. Work by Giorgi et al,¹⁰ who plotted critical temperature of NbC and TaC as a function of carbon content showed increasing critical temperature as the carbon content approached 50 at. %.

II. EXPERIMENTAL PROCEDURE

Commercially prepared powders of TaC and NbC were obtained from Fansteel Metallurgical Corporation. Lattice parameters, obtained from x-ray diffraction studies of the powders, showed the tantalum carbide¹¹ to have the formula TaC_{.98} and the niobium carbide¹² to be NbC_{.96}. From the work of Giorgi et al¹⁰, both compounds were expected to have critical temperatures near 9.5°K.

In order to reduce particle size, the powders were ball-milled for 72 hours in toluene as a dispersing agent. They were then dried and leached with HCl to remove any iron contamination from the milling process. Distilled water was used to remove soluble chlorides. The carbide powders, dried with alcohol and acetone, were mixed by dry tumbling in proportions covering the entire solid solution range of the system.

Samples were extruded as 1/8" rods with styrene as a binder. A solution of 3% styrene in toluene was added to the dry mixed powders. Then the toluene was evaporated leaving the carbide particles coated with styrene. Diphenyl was added as a plasticizer, and the mixture was heated to 160°C for the extrusion process.

The initial heating cycle was carried out at relatively low temperatures. The temperature was raised to 375°C over a period of four hours and held constant for another four hours. During this time the styrene binder volatilized into an atmosphere of purified (dried and deoxygenated) helium.

Further heating was carried out in vacuum. The temperature was raised to 1350°C over a four hour period and was held at that temperature for another four hours. The furnace was allowed to cool to room

temperature before the samples were removed. After this initial firing the samples were very fragile but had sintered to some extent. The final firing, also in vacuum, was at 2100°C for periods ranging from 3 to 60 hours. Critical temperature measurements were made by observation of the temperature at which the impedance changed in a coil surrounding the sample.¹³

Those samples which had been fired for relatively short times showed very broad superconducting transitions. X-ray diffraction patterns showed some lines from the pure components, indicating inhomogeneity.

Samples fired at 60 hours had superconducting transitions over a temperature range of 3 to 4°C. Giorgi, in a private communication, indicated that the width of the transition may be due to departure from stoichiometry.

III. RESULTS

Figure 8 shows the experimental results of critical temperature plotted as a function of composition. In order to verify that this maximum in temperature is not due to a change in stoichiometry, lattice parameters were measured on all samples. The lattice parameter varied linearly with composition (Fig. 9).

Powders of unmixed TaC and NbC were also extruded and fired with the same procedure used in preparation of the solid solutions. These samples showed the same lattice parameter and critical temperature as the unprocessed powders, indicating that the preparation procedure did

not significantly contaminate the specimens.

IV. DISCUSSION

Studies have been made of critical temperature as a function of composition in other carbide systems. The systems of MoC with NbC, TiC, ZrC, and VC were studied over the range of cubic solid solutions.¹⁴ MoC is normally hexagonal but forms cubic solid solutions up to 80% MoC. Critical temperature plotted as a function of composition extrapolated to 10.3°K, the transition temperature of the hypothetical cubic form of MoC. All curves except MoC-NbC were monotonically decreasing with decreasing amounts of MoC. The MoC-NbC was the only solid solution system studied which was composed of two superconductors. This system showed a maximum critical temperature higher than that of either pure content.

Another system that has been studied is HfN-ZrN.¹⁵ This system is also formed from two superconductors, but the critical temperature varies smoothly from the critical temperature of one component to that of the other without showing a maximum.

The results of the present study show that, while critical temperature has been successfully related to crystal-chemical properties in the Al₅ structure, such empirical correlations are unsuccessful in studies of the B1 structure. A linear variation in lattice parameter should predict the highest critical temperature for TaC, the component with the smallest lattice spacing. This prediction was shown to be incorrect. Therefore, the rules so successfully applied to the Al₅ structure are insufficient criteria for superconductivity in the B1 class of superconducting compounds.

V. FUTURE WORK

Future work is being planned to study solid solutions of carbides and nitrides of vanadium, niobium, and tantalum. Of these compounds, TaN and VC are non-superconducting. Critical field studies and specific heat measurements of these systems will also be made.

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FIGURE CAPTIONS

1. A sample which becomes a perfect conductor after being placed in a magnetic field traps the lines of magnetic flux after the field is removed.
2. A perfect conductor completely excludes magnetic flux.
3. At absolute zero and at the critical temperature the entropies of the normal and superconducting phases are zero. There is a finite difference in the specific heats of the two phases at the critical temperature.
4. The Al₅ structure consists of body centered cubic A atoms with B atoms in mutually perpendicular, non-intersecting chains on the cube faces.
5. Maximum critical temperature in the Al₅ structure occurs at the maximum mean atomic volume with the exception of V₃Si and its modifications.
6. Maximum critical temperatures in the Al₅ structure occur at 4.7 and at 6.5 valence electrons per atom.
7. Certain values of electrons per cubic Angstrom are particularly favorable for superconductivity.
8. Critical temperature plotted as a function of composition in the TaC-NbC shows a maximum.
9. Lattice parameters in the system of TaC-NbC solid solutions varies linearly with composition.

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Fig. 1

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Fig. 2

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Fig. 3

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Fig. 4

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Fig. 5

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Fig. 6

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Fig. 7

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Fig. 8

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Fig. 9

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