tion this term involves only the optical lattice vibrations. It is possible that future investigation will reveal that a similar contribution involving the acoustical lattice vibrations must be taken into account. In any case, however, such a term would not affect the qualitative conclusions which are made above, but would affect their quantitative interpretation.

VI. ACKNOWLEDGMENTS

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The Superconductivity of Some Transition Metal Compounds*

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About eighty transition metal compounds comprising borides, carbides, nitrides, oxides, silicides, and germanides of metals of Groups 4A, 5A, and 6A were tested for superconductivity down to 1.20°K, using a magnetic method. Among the specimens were most of the known compounds of the above type not examined magnetically for superconducting behavior by previous workers, and in all cases the structures were checked by x-ray diffraction analysis. The following eleven new superconductors were discovered, with the transition temperatures (°K) shown in parentheses: W_2B (3.10°), Nb_2C (9.18°), Ta_2C (3.26°), Nb_4N_3 (7.2°), V_3Si (17.1°), V_3Ge (6.01°), Mo_3Si (1.30°), Mo_3Ge (1.43°), α-$ThSi_2$ (3.16°), β-$ThSi_2$ (2.41°), and W_3Si_2 (2.84°). These compounds include the first superconducting germanides, V_3Ge and Mo_3Ge, which, together with V_3Si and Mo_3Si, crystallize in the cubic β-tungsten structure. The transition temperature of V_3Si is apparently the highest known for any binary superconducting compound.

I. INTRODUCTION

It is well known that there exists a group of compounds of transition metals with nonmetals, typified by the borides, carbides, and nitrides of "A group" transition metals, which possess most of the properties of metals or alloys. These compounds show metallic luster and have thermal and electrical resistivities of the same order of magnitude as those for pure metals, together with a positive temperature coefficient of electrical resistivity. In many cases they are known to have high hardness values, high moduli of elasticity, high melting points, and relatively high strengths at elevated temperatures, properties which cause them to be of considerable technological importance.[1] At the time of the first extensive crystal structure determinations for these substances, carried out by Hägg,[2] it seemed appropriate to call them "interstitial" compounds, implying that the nonmetal atoms merely fit into interstices in the metallic lattice, thereby slightly modifying the properties of the pure metal. More recent investigations have shown that for borides the interstitial picture is inadequate owing to the tendency of the boron to form chains, nets, and three-dimensional networks,[3] while even for carbides and nitrides it is the exception rather than the rule for the lattice of metal atoms in the compound to be identical with the lattice of the pure metal.[4]

Among the typically metallic properties of transition metal compounds one may include the fact that many become superconducting at temperatures of a few degrees absolute. This behavior was first discovered during the extensive investigations of Meissner and his co-workers over twenty years ago.[5–7] Unfortunately, Meissner's results were obtained using electrical resistance measurements, which have since been shown to yield unreliable results with impure specimens. The

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[1] The term "hard metals" is often applied to this whole group of materials. See P. Schwarzkopf and R. Kieffer, *Refractory Hard Metals* (Macmillan Company, New York, 1953).

[2] G. Hägg, Z. physik. Chem. **B6**, 221 (1930); **B12**, 33 (1931).

[3] R. Kiessling, Acta Chem. Scand. **1**, 893 (1947); **3**, 90 and 595 (1949); **4**, 146 and 209 (1950).

[4] R. E. Rundle, Acta Cryst. **1**, 180 (1948).

[5] W. Meissner and H. Franz, Z. Physik **65**, 30 (1930).

[6] Meissner, Franz, and Westerhoff, Ann. Physik **13**, 505 (1932); **17**, 593 (1933).

[7] Meissner, Franz, and Westerhoff, Z. Physik **75**, 521 (1932).

problem has recently been taken up by several other investigators[8–10] using more decisive magnetic methods; these experiments have revealed a number of new superconducting compounds, and have corrected several errors in the earlier work.

In spite of the increased interest in this field, the results reported to date have been confined mainly to the borides, carbides, and nitrides of the "A group" transition metals and even here have not covered all of the known compounds. Since these data are important for the light which they may throw on the fundamental chemical and crystallographical conditions favoring the occurrence of superconductivity, we have felt that it would be of value to complete and extend them as far as possible. Using a magnetic method for the detection of superconductivity, we have studied a number of borides, carbides, nitrides, and oxides which have not previously been tested for superconducting behavior, and have reinvestigated several compounds of this type already tested by previous workers. We have also systematically surveyed the occurrence of superconductivity among the silicides and germanides of the "A group" transition metals, since these compounds have been largely neglected in previous superconducting work, although they have received much study from the metallurgical standpoint. While many of our data on the latter compounds have already been briefly reported,[11] the present paper describes the experimental techniques used and the detailed structural and superconducting results so far obtained.

II. EXPERIMENTAL DETAILS

A. Method

Superconductivity is most simply detected by measuring either the electrical resistance or the magnetic permeability of a given specimen. The ideal specimen for both these tests is a long solid rod of pure, homogeneous, strain-free material; for such a specimen the electrical resistivity and magnetic permeability in a small field may both be expected to drop to zero rather sharply as the temperature is lowered through the superconducting transition point.[12] Unfortunately, since most of the compounds with which the present work is concerned exhibit such properties as high melting points, brittleness, and ease of contamination, the fabrication of an ideal specimen of the above type is, with present techniques, a very tedious and difficult task. Thus, in preliminary experiments it is necessary to work with more readily prepared specimens, which, for the refractory compounds, include arc-melted pellets, porous sintered rods, or even fine powders. For these specimens the onset of superconductivity is often smeared out over a range of temperature, but a large drop in resistance or permeability usually gives unmistakable evidence of superconducting behavior.

Some caution is necessary in interpreting the results on inhomogeneous specimens, for the following reasons. It is not infrequent for such specimens, even when carefully prepared, to contain small amounts of superconducting impurities, often as one or more separate phases. Small quantities of the latter will sometimes form a continuous path through the specimen, for example at the grain boundaries, and cause the apparent resistance of the entire specimen to disappear at the transition point of the impurity.[13] Alternatively, the impurity may be deposited in a thin skin around the individual grains or particles of the specimen; if the thickness of this skin exceeds the penetration depth ($\sim 10^{-5}$ cm), the onset of superconductivity in the impurity is accompanied by the exclusion of magnetic flux from the grain or particle as a whole, so that the impurity produces a much greater magnetic effect than one might expect from its actual volume. Thus, in both electrical and magnetic tests for superconductivity it is essential to take account of impurities, even trace amounts, in the specimens. Failure to observe this point in early work led to a number of ambiguities, some of which crop up in the present investigation. However, the difficulties resulted mainly from resistance tests, which are apparently more sensitive to impurities than magnetic tests, presumably because continuous filaments are formed more readily than closed skins. For this reason, and also because of the unsuitability of the resistance method for powdered samples, the magnetic method is preferred in the present work.

B. Apparatus

The magnetic test arrangement used in earlier work[9] was supplemented by a new gas thermometer cryostat in which specimens could be studied not only in the liquid hydrogen and liquid helium ranges, but also at accurately known temperatures in the intervening region. The essential low-temperature parts of this apparatus are shown in cross section in Fig. 1. For simplicity, the surrounding liquid nitrogen Dewar flask and the head of the cryostat with its associated electrical connections and pumping lines are omitted from the diagram.

The six specimens which could be tested during a single experiment were mounted in radial positions just inside the rim of a hollow copper spool, which also served as a gas thermometer bulb *D*. The top and bottom plates of the spool were slotted radially to minimize magnetic disturbance due to eddy currents.

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[8] F. H. Horn and W. T. Ziegler, J. Am. Chem. Soc. **69**, 2762 (1947).

[9] B. T. Matthias and J. K. Hulm, Phys. Rev. **87**, 799 (1952).

[10] W. T. Ziegler and R. A. Young, Phys. Rev. **90**, 115 (1953).

[11] G. Hardy and J. K. Hulm, Phys. Rev. **89**, 884 (1953).

[12] See D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), second edition.

[13] D. Shoenberg, Nature **159**, 303 (1947).

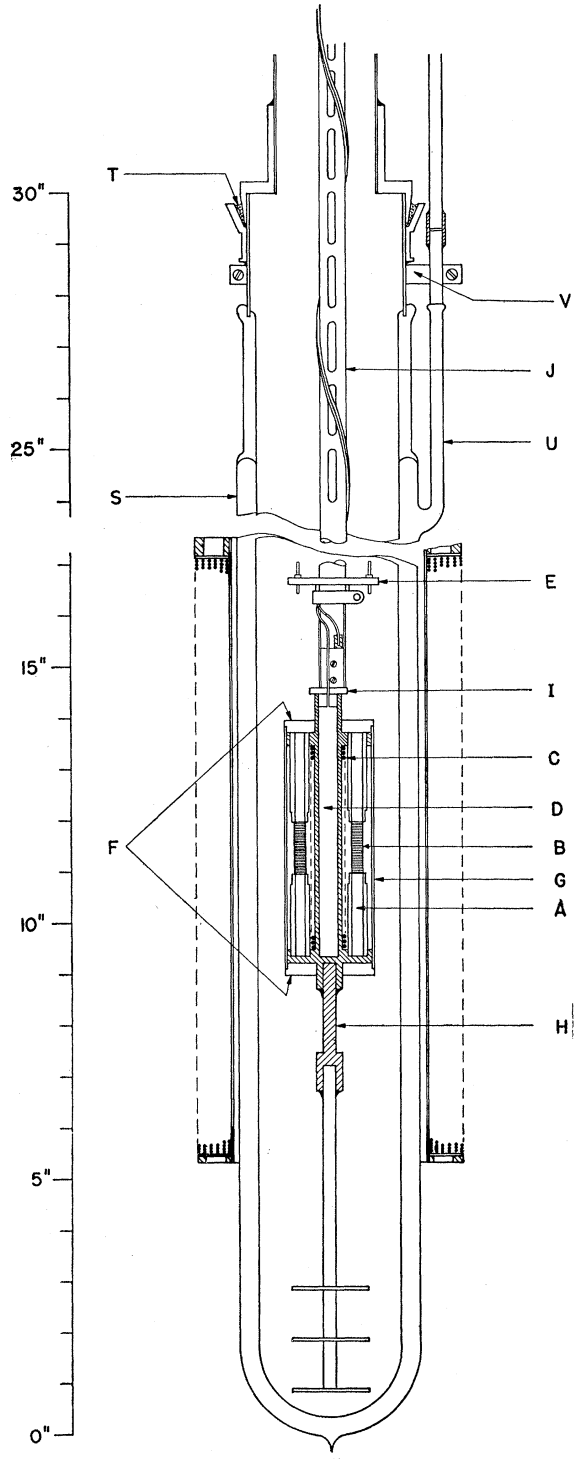

FIG. 1. Gas thermometer cryostat (lower half), liquid nitrogen Dewar flask removed.

Fragmented or powdered specimens and sintered rods were contained in Lucite tubes *A*, each having a thin-walled section upon which a detector coil *B*, consisting of about 250 turns of 40-gauge Formex insulated copper wire, was tightly wound. Melted pellets were held in position in the spool by micarta supports and had detector coils wound directly upon them. Leads from the six coils passed out of the cryostat via the terminals *E* and were connected through a selector switch to an almost critically damped ballistic galvanometer. Uniform magnetic fields up to about 700 oersteds could be applied to the specimens by a liquid-nitrogen-cooled solenoid which was suspended outside the liquid helium Dewar flask *S* but inside the liquid nitrogen flask. The Pyrex helium Dewar was itself attached to the cryostat head by a copper-to-glass seal and an easily disconnected Rose's metal joint *T*, while the interspace could be evacuated through the tube *U* and an external needle valve.

C. Temperature Measurement

For measurements below 4.2°K, the specimen holder was completely submerged in liquid helium; temperatures down to just below 1.2°K could be attained by suitably varying the pumping rate on the liquid helium bath. In this range the specimen temperatures were obtained by measuring the vapor pressure of the bath, using for conversion the 1949 International Scale.[14] A similar procedure was used in the liquid hydrogen range.

For measurements between 4.2°K and 13.9°K the triple point of liquid hydrogen, the helium bath level was allowed to fall below the specimen holder. The temperature of the specimen holder was then raised above that of the bath by means of a heater coil *C* of 30-gauge manganin wire wound noninductively upon the outside of the gas thermometer bulb. Heat from this coil flowed down a brass rod *H* and was dissipated in the helium bath via a copper fin system which extended to the bottom of the Dewar. Owing to the high thermal conductivity of copper relative to that of brass, almost the entire temperature drop occurred in the brass rod and the gradient in the specimen holder was negligible. In addition, the slotted support tube *J* of Supernickel ensured that the heat input from the cryostat head was negligible compared to that generated in the heater coil, while a thin brass envelope *G* and Lucite end plates *F* prevented convection in the helium vapor from disturbing the temperature equilibrium of the specimens.

Specimen temperatures above 4.2°K were measured with the constant volume helium gas thermometer (bulb *D*) which had previously been calibrated when immersed in liquid helium. After corrections for dead-space volume, gas imperfections, and thermomolecular pressure gradient in the capillary tube, specimen temperatures between 4.2° and 13.9°K were known to better than 0.01°K. This accuracy was checked in two ways, first by using the gas thermometer to investigate certain superconducting transition curves which lay

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[14] H. Van Dijk and D. Shoenberg, Nature **164**, 151 (1949).

above 13.9°K and which had previously been studied by immersing the specimens directly in liquid hydrogen, and second by comparing our results for a single crystal of lead with those of previous workers.[15] In both cases the specimen temperatures agreed to within one hundredth of a degree, while temperature inequalities within the specimens could be presumed to be even smaller than this value.

D. Magnetic Measurements

Prior to each experiment the magnetic system was calibrated at room temperature by observing the galvanometer throw from each detector coil due to switching off an accurately known solenoid field of a few oersteds. This procedure was carried out first with the coils empty and second with the specimens in place, in order to show up ferromagnetic or other anomalous magnetic properties. In most cases, however, there was no noticeable difference between the "full" and "empty" readings, indicating a specimen permeability close to unity. Morever, the galvanometer throw was quite accurately proportional to the applied field for fields up to a few hundred oersteds.

On cooling to liquid hydrogen or liquid helium temperatures, there was always a small, reproducible increase in deflection per unit change of field, presumably due to small changes in the detector coil dimensions and circuit resistance. When the specimen became superconducting, however, a large decrease in deflection was observed such as shown in Fig. 2. In this diagram the effective permeability μ is the ratio of the actual deflection due to switching off a given field H' to the deflection obtained in the normal region by switching off the same field. Initial tests showed that the deflection given by each coil was unaffected by the presence of superconductors in any of the five remaining coils within the specimen holder.

The onset of superconductivity usually took place over an appreciable range of temperature, as shown in Fig. 2; such transition broadening is thought to be mainly due to inhomogeneities in composition and strain which produce variations of transition temperature from one region of the specimen to another. Thus, as will be seen later, very wide transitions, spread over a degree or more, were observed for certain carbides and nitrides in which quite large variations of carbon and nitrogen content are known to be possible. On the other hand, much sharper transitions were found for most of the silicides and germanides in which far smaller deviations from stoichiometric composition are permitted. Assuming that the variations of composition throughout a specimen are mainly random deviations from an ideal, stoichiometric formula, it seems reasonable to obtain the transition temperature from the mid-point of the transition curve, corresponding to an effective permeability $(\mu_0+1)/2$, where $\mu \rightarrow \mu_0$ as $T \rightarrow 0$. Most of our data were treated in this fashion, but in a few cases, for example certain nitrides, where most of the spreading was attributable to a specific dissolved impurity which displaced T_c in one direction, the transition temperature was estimated from the point of onset of superconductivity in the purest sample.

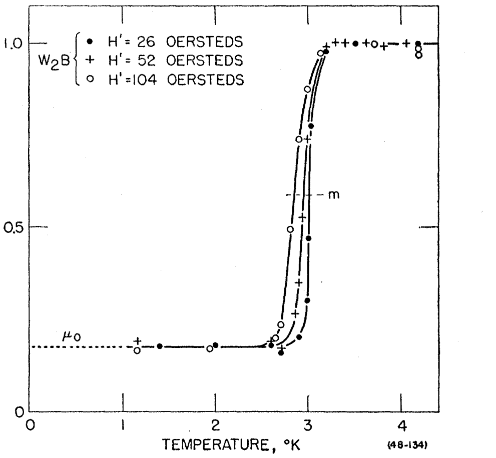

FIG. 2. Temperature variation of effective permeability at various values of measuring field H' arc-melted W_2B specimen.

A slight broadening of the transition occurs for purely geometrical reasons when the specimen does not have the ideal long, cylindrical shape. Thus, for an ellipsoid of demagnetizing coefficient $4\pi n$ in a measuring field H' small compared to the critical field at absolute zero H_{c0}, it may be shown that the mid-point of the transition T_m and its total breadth ΔT are given by

$$T_m/T_c = 1-\tfrac{1}{4}[(2-n)/(1-n)][H'/H_{c0}] \qquad (1)$$

and

$$\Delta T/T_c = \tfrac{1}{2}[n/(1-n)][H'/H_{c0}], \qquad (2)$$

respectively. The first equation indicates that T_m always depends upon H', even for an ideal, cylindrical specimen with zero n; a linear dependence of this type was in fact observed for all our specimens (e.g., Fig. 2), and each transition temperature was determined from the value of T_m obtained at several different field strengths by extrapolating to zero field. Since our estimated n values rarely exceeded one-third (the value for a sphere) and H'/H_{c0} could usually be assumed to be less than 0.1, the geometrical transition width was less than $T_c/40$ which was in most cases negligible compared to the broadening due to inhomogeneity. Owing to the nonideal nature of the specimens, no accurate values of H_{c0} were obtained in the present work.

The effective permeability of our specimens in the limit $T \rightarrow 0$, μ_0, was never actually zero, for several reasons. First, there was flux leakage between the windings of the detector coil and the specimen and also through the specimen itself in the case of powders or

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[15] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. (London) **A160**, 127 (1937).

sintered rods. Second, it was often necessary to work with specimens containing substantial amounts of other phases besides the compound of chief interest. Where these impurity phases were known to be normal down to 1.20°K, they merely served further to dilute the specimens and to increase μ_0. For superconducting impurities, however, the situation was less clear owing to the possibility of an anomalous decrease in μ_0 due to magnetic shielding of the type discussed in II A. Fortunately, it was almost always possible to exclude such impurities in our work, and there were only three cases[16] in which a large magnetic effect could perhaps be attributed to a minor superconducting phase.

E. Specimen Preparation

The borides, carbides, and monoxides tested were, in most cases, prepared by the fusion of compressed pellets consisting of appropriate mixtures of the pure powdered metals with boron, carbon, or higher metallic oxide powders in an arc-melting furnace. Melting was carried out in an atmosphere of specially purified argon. The pellets were melted repeatedly, using a tungsten electrode, in a water-cooled copper crucible; spectrographic analyses of representative specimens showed that the copper and tungsten pickup of the arc-melts was considerably less than 0.1 percent in all cases. When phases that formed only at very high temperatures were not under investigation, the specimens were then annealed at about 1500°C for between 20 and 50 hours in an atmosphere of purified helium.

Most of the silicides were prepared by heating compressed pellets of the powdered metals and silicon for several hours at about 1500°C in a furnace heated by "Globar" resistance elements. The pellets were supported by "Alundum" boats placed in the center of the "Sillimanite" furnace tube in which a slight overpressure of pure helium was maintained during heating. Many duplicate silicide specimens were prepared by arc-melting, and gave in most cases superconducting results practically identical with those obtained for sintered specimens of the same composition.

Germanide specimens were also prepared by the sintering technique, compressed pellets of germanium and metal powders being heated at about 1000°C in pure helium gas. Arc-melting preparations were tried for many of these compounds, but were usually unsuccessful due to extensive volatilization of germanium. In particular, we were unable to obtain suitable specimens of the lower niobium and tantalum germanides for this reason; these specimens could not be prepared by sintering even after very extended periods, since the inertness of the metals caused spongy, extremely inhomogeneous specimens to be produced.

Nitride preparations were usually carried out in a second "Globar" furnace in which metal powders could be heated to about 1450°C in carefully purified nitrogen. In one case, vanadium nitride, the compound was obtained by decomposing ammonium metavanadate in a stream of dry ammonia.

The composition of all specimens was checked by by x-ray powder diffraction analysis, and lattice parameter determinations were carried out wherever feasible. The results were for the most part in good agreement with those of earlier workers[17] and need not be discussed in great detail. Our structural data will be mentioned explicitly only in cases of appreciable deviation from earlier work or where new phases were observed. When the exact composition or the very existence of a phase is in doubt, the formula appears in quotation marks.

Spectrographic analyses showed that most of the specimens contained less than 0.1 percent of dissolved metallic impurities, and here again the exceptions are discussed later. Finally, vacuum fusion analyses were performed in an iron bath at about 2100°C for most of the nitrides and proved essential in relating the oxygen and nitrogen contents of these specimens to their superconducting behavior.

III. RESULTS AND DISCUSSION

A. Borides

Of eighteen transition metal borides tested magnetically by Matthias and Hulm,[9] only two, NbB and Mo_2B, were superconducting above 1.28°K. Ziegler and Young[10] reported normal behavior in seven borides down to 1.8°K. Among the remaining borides we have tested the nine compounds TiB, "ThB," "V_2B" (two forms), VB, Ta_2B, Cr_2B, W_2B, and Ru_2B down to a temperature slightly below 1.20°K. The results for these compounds are summarized in Table I (super-

TABLE I. Superconducting nitrides, carbides, and borides of the Groups 4, 5, and 6 transition metals.

TiN (5.6°)[a]	VN (8.2°)[a]	None reported for chromium
ZrN (8.9°)[a]	Nb_4N_3 (7.2°)[a]	Mo_2N (5.0°)[d]
["ZrB" (3.3°)][b]	NbN (14.7°)[c]	MoN (12.0°)[d]
	Nb_2C (9.18°)[a]	Mo_2C (2.78°)[d]
None reported for hafnium or the lanthanide and actinide series of metals	NbC (6.0°)[a]	MoC (9.26°)[d]
	NbB (8.25°)[d]	Mo_2B (4.74°)[d]
	Ta_2C (3.26°)[a]	W_2C (2.74°)[d]
	[Ta_2B (3.12°)][a,e]	W_2B (3.10°)[a]

[a] Transition temperature from present work, magnetic data.
[b] Transition temperature from reference 7, electrical data only.
[c] Transition temperature from reference 8, magnetic data.
[d] Transition temperature from reference 9, magnetic data.
[e] Superconductivity doubtful owing to free tantalum (see text).

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[16] Ta_2B, "Nb_2Ge," and "Ta_2Ge" specimens all contained traces of free metal (see later discussion).

[17] The literature on the crystal structure and phase diagram constitution of the transition metal borides, carbides, nitrides, and silicides is very extensive, but, fortunately a comprehensive survey of this field has recently been published (reference 1). The present paper does not, therefore, include an exhaustive list of all the references consulted in connection with our chemical and structural studies, and specific mention is made only of very recent publications or those articles having close bearing on the superconductive investigation.

TABLE II. Nonsuperconducting borides, carbides, nitrides, and oxides of the Groups 4, 5, and 6 transition metals.

TiB^a	"V_2B" $(2)^a$	Cr_2B^a
$TiB_2{}^{b,c}$	VB^a	CrB^b
$TiC^{a,c,d}$	V_2C^a	$CrB_2{}^b$
TiO^a	$VC^{a,c,d}$	Cr_4C^a
	"V_5N_2"^{a}	$Cr_7C_3{}^a$
	VO^a	$Cr_3C_2{}^{a,b}$
		CrN^b
$ZrB_2{}^c$	$Nb_3B_4{}^b$	
$ZrC^{a,c,d}$	$NbB_2{}^{b,c}$	MoB $(2)^{b,c}$
	Nb_2N^a	$Mo_2B_5{}^b$
	$NbO^{a,d}$	
HfB^d		$WB^{b,c}$
HfC^d	TaB^b	$W_2B_5{}^b$
	$Ta_3B_4{}^b$	$WC^{b,c}$
"ThB"^{a}	$TaB_2{}^{b,c}$	W_2N^b
$ThB_2{}^c$	$TaC^{a,c}$	
ThC^a	$Ta_2N^{a,e}$	UC^a
$Th_3N_4{}^a$	$TaN^{a,e}$	UN^a

[a] Tested magnetically down to 1.20°K, present work.
[b] Tested magnetically down to 1.28°K, reference 9.
[c] Tested magnetically down to 1.8°K, reference 10.
[d] Tested electrically down to about 1.2°K, references 5–7.
[e] Tested magnetically down to 1.88°K, reference 8.

conducting) and Table II (normal), together with our data for carbides, nitrides, and oxides of the transition metals discussed in later sections. These tables also show the borides, carbides, and nitrides tested by earlier workers, classified according to the best available evidence.

Of the compounds tested by us, only Ta_2B and W_2B showed superconducting behavior, the latter exhibiting a fairly sharp transition (Fig. 2) centered on 3.10°K. Unfortunately, in common with previous investigators,[3,18] we were unable to prepare a specimen of Ta_2B which did not contain substantial amounts (about 30 percent of each) of free tantalum and TaB, even though a number of different annealing procedures were tried. These specimens all showed superconductivity at about 3.12°K. In spite of the very high flux expulsion from the detector coil (about 80 percent), it was felt, for the reasons discussed in Sec. II, that the magnetic effect could be due to the free tantalum in the specimens. This view was supported by the data for an arc-melted specimen of tantalum saturated with boron, which had a transition temperature of 3.32°K. Thus, although Ta_2B itself may become superconducting close to 3°K, this result is not definitely established.

The normal compounds include the recently reported phase VB;[19] and two new phases which were observed in several specimens of the over-all composition V_2B prepared by arc-melting, followed by prolonged annealing, in some cases, at temperatures of 1500° and 1700°C. These specimens were shown by x-ray diffraction analysis to contain two new compounds of unknown crystal structure. Only one of these phases was present in the unannealed arc-melts; all of the annealed specimens contained both phases in roughly equal amounts.

The specimen of Ru_2B[20] was prepared by melting together the elements under pure helium at 1450°C, followed by twelve hours' annealing at 1100°C. The complex x-ray diffraction pattern of this compound has not been interpreted; the x-ray data showed, however, that our specimen contained no RuB or free ruthenium.

Several attempts were made to prepare the monoboride of zirconium, which has recently been investigated by Post and Glaser.[21–23] This compound is of special interest in view of Meissner, Franz, and Westerhoff's earlier result[7] that the electrical resistance of "ZrB" drops to zero between 3.8° and 2.8°K. Since "ZrB" is reported as forming only between 1000° and 1200°C, our preparations were carried out in a vacuum induction furnace or in the annealing furnace. All of the resulting specimens proved to contain only Zr, ZrB_2, and traces of ZrO_2, so that the superconductivity of zirconium monoboride could not be checked.

Magnetic data are now available for four hemiborides which crystallize in the tetragonal $CuAl_2[D_{4h}{}^{18}]$ type of lattice, namely, Mo_2B and W_2B (superconducting), Ta_2B (doubtful), and Cr_2B (normal to 1.2°K). Including, as it does, two of the three known superconducting borides, this lattice evidently favors superconductivity, perhaps because the individual boron atoms are isolated. One might expect the higher borides to be somewhat less "metallic" in character owing to the progressive increase in the number of covalent linkages between boron atoms with increasing boron content,[24] although it must be admitted that this change does not seem to be accompanied by a systematic increase in electrical resistivity.[1,22] Another interesting feature is that the known superconducting borides are clustered in a single region of the periodic system in which two of the parent metals, molybdenum and tungsten, remain normal down to very low temperatures. This situation will shortly be seen to be repeated, with some variations, in several other classes of compounds.

B. Carbides

Meissner and his co-workers[5,7] observed that the electrical resistance of monocarbide specimens of ZrC, NbC, TaC, MoC, and WC dropped steeply, in some cases to zero, in the temperature intervals 4.07°–3.35°, 10.5°–10.1°, 9.5°–9.3°, 7.8°–7.6°, and 4.2°–2.5°K, respectively. However, in magnetic measurements

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[18] Brewer, Sawyer, Templeton, and Dauben, J. Am. Ceram. Soc. **34**, 173 (1951).

[19] H. Blumenthal, J. Am. Chem. Soc. **74**, 2942 (1952), reported VB as isomorphous with CrB (Orthorhombic $D_{2h}{}^{17}$), lattice parameters 3.10, 8.17, and 2.98A. We had independently reached the same conclusion and found the lattice parameters 3.058, 8.026, and 2.971A.

[20] J. H. Buddery and A. J. Welch, Nature **167**, 362 (1951).

[21] B. Post and F. W. Glaser, J. Chem. Phys. **20**, 1050 (1952).

[22] F. W. Glaser, J. Metals **4**, 391 (1952).

[23] F. W. Glaser and B. Post, J. Metals **5**, 1117 (1953).

[24] R. Kiessling, J. Electrochem. Soc. **98**, 166 (1951).

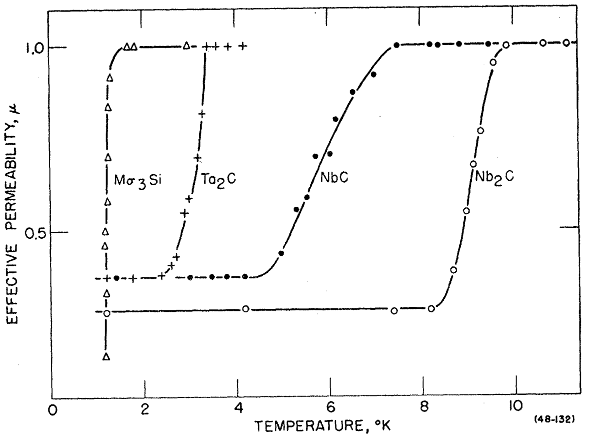

Fig. 3. Temperature variation of effective permeability for arc-melted Nb_2C, NbC, Ta_2C, and sintered Mo_3Si specimens, measuring field 26 oersteds.

Ziegler and Young[10] found no evidence of superconducting behavior in TiC, ZrC, VC, TaC, and WC down to 1.8°K, while Matthias and Hulm[9] reported WC to be normal down to 1.28°K, but MoC as superconducting at about 9.26°K, which is somewhat higher than Meissner and Franz's value.

To check and extend these results we studied the seven monocarbides TiC, ZrC, ThC, VC, NbC, TaC, and UC down to 1.20°K. Most of these compounds were prepared by arc-melting, but the specimen of UC was obtained in a vacuum induction furnace by the reaction at 1800°C of an intimate mixture of U_3O_8 and graphite powder, contained in a graphite crucible.[25,26] This method of preparation might be expected to yield a product containing appreciable amounts of oxygen in solution; unfortunately, the previously reported values[25,26] of the lattice constant of "pure" UC differ by 0.004A, with the result that the lattice paremeter for our specimen (4.952A), while it lay between the two published values, did not provide a very precise indication of the specimen purity. The specimens of ThC and UC, both of which are unstable in air, were handled in a dry-box under argon, and were tested while sealed in thin-walled glass tubes under pure helium.

No evidence of superconducting behavior was found in the monocarbides of titanium, zirconium, thorium, vanadium, tantalum, and uranium, so that we must conclude, in agreement with Ziegler and Young,[10] that the disappearance of electrical resistance found by Meissner and Franz in ZrC and TaC was due to traces of superconducting impurity, possibly the nitride in the former case and free tantalum in the latter. Our NbC specimen showed a rather broad superconducting transition over a range of about 3°K with its mid-point at 6°K (Fig. 3). Since the x-ray diffraction pattern of this specimen contained only monocarbide lines, we presume that the electrical transition which Meissner and Franz[5] found between 10.5° and 10.1°K for "NbC" may have been due to impurities, perhaps Nb_2C (see below) or free niobium.

In addition to the monocarbides, we investigated the lower compounds V_2C, Nb_2C, Ta_2C, Cr_4C, Cr_7C_3, and Cr_3C_2 down to 1.20°K. Since Cr_4C was reported[27] to be unstable above 1530°C, this specimen was annealed at about 1450°C for 50 hours, after arc-melting. Nb_2C and Ta_2C were also subjected to a similar, especially long annealing treatment and their x-ray diffraction patterns contained no lines due to other compounds or to the free metals. It should be mentioned that although the hemicarbides of vanadium and niobium have been reported by several workers,[28–31] some doubt has been expressed regarding their actual existence.[32] However, our x-ray data for these compounds indicated a hexagonal structure, similar to that of Ta_2C, Mo_2C, and W_2C, with the lattice parameters 2.944, 4.608A (V_2C) and 3.105, 4.970A (Nb_2C).

Of the six lower carbides tested, only Nb_2C and Ta_2C became superconducting above 1.20°K; both these compounds exhibited quite sharp transitions centered upon 9.18°K (Nb_2C) and 3.26°K (Ta_2C) (Fig. 3). Neither compound has been investigated for superconductivity in previous work.

C. Nitrides

Electrical resistance transitions similar to those found by Meissner and his co-workers in the monocarbides were also reported by these investigators for the mononitrides TiN (two drops in resistance, at 5.5° and 1.2°K), ZrN (9.6°–9.3°K), and VN (3.2°–1.5°K). More recently, Justi and his co-workers[33] and Horn and Ziegler[8] independently found magnetic evidence of superconductivity in NbN at about 15°K, while the latter workers reported TaN as normal down to 1.88°K.

TABLE III. Influence of oxygen contamination on the superconductivity of TiN.

Specimen	Oxygen content (weight %)	Lattice parameter (A)	T_c[a] (°K)
A	0.4	4.240	5.58
B	0.8	4.240	5.58
C	1.5	4.240	4.86
D	1.6	4.230	2.90

[a] Onset temperature, extrapolated to zero field.

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[25] Rundle, Baenziger, Wilson, and McDonald, J. Am. Chem. Soc. **70**, 99 (1948).

[26] Litz, Garrett, and Croxton, J. Am. Chem. Soc. **70**, 1718 (1948).

[27] See M. Hansen, *Der Aufbau der Zweistofflegierungen* (Julius Springer, Berlin, 1936), p. 354.

[28] A. Westgren, Metallwirtschaft **9**, 921 (1930).

[29] M. Oya and A. Osawa, Sci. Repts. Tôhoku Univ. **19**, 95 (1930).

[30] G. Brauer, Z. Elektrochem. **46**, 397 (1940).

[31] J. S. Umanski, Zhur. Fiz. Khim. **14**, 332 (1940).

[32] See reference 1, pp. 104, 110.

[33] Aschermann, Friederich, Justi, and Kramer, Physik. Z. **42**, 349 (1941).

Matthias and Hulm[9] observed a superconducting transition in MoN at about 12°K.

Since the electrical data for several monocarbides were not confirmed by later magnetic tests, it was felt necessary to check the above electrical results for the mononitrides. While our magnetic studies have shown that all three compounds, TiN, ZrN, and VN, are indeed superconducting, the behavior of our specimens of TiN and VN was found to be quite sensitive to variations in the small quantities of oxygen which entered the specimens during preparation.

By heating various samples of titanium for about 8 hours at 1450°C in nitrogen gas subjected to different degrees of purification, we prepared three specimens of TiN (*A*, *B*, and *C*) containing slightly different amounts of oxygen. The oxygen contents determined by vacuum fusion analysis are shown in Table III and the superconducting results in Fig. 4. X-ray evidence ("tailing" off of diffraction peaks at high angles) and slight changes of color from the surface to the interior of these specimens suggested that the oxygen content was somewhat higher in the surface region than at the center. This was also supported by the very wide range of the superconducting transition; the sharp drop in permeability at about 5.5°K for specimen *A* is attributed to a pure central core in which the oxygen content was even less than the 0.4 percent average value for the specimen as a whole. It should be noted that the same lattice parameter was obtained for *A*, *B*, and *C*, 4.240A, which lies between the values 4.242A and 4.235A reported previously for pure TiN.[34,35]

As a further check on the above results, a fourth TiN specimen, *D* (Table III), was prepared by annealing part of specimen *C* under purified helium for twenty hours at 1500°C. The total oxygen content was hardly changed, but, presumably owing to diffusion of oxygen into the purer parts of the specimen, the lattice parameter decreased appreciably and the temperature of onset of superconductivity (not shown in Fig. 4) was depressed to 2.9°K. Replacement of nitrogen by oxygen in the TiN lattice evidently decreases the superconducting transition temperature, which is not unreasonable in view of the fact that the isostructural monoxide, TiO, is itself normal down to 1.20°K (Sec. III D).

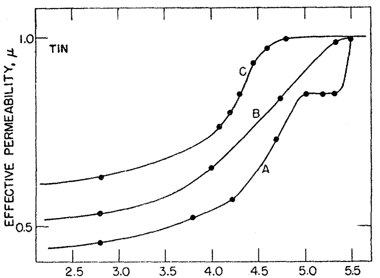

FIG. 4. Temperature variation of effective permeability for sintered TiN samples containing different amounts of oxygen (Table III), measuring field 26 oersteds.

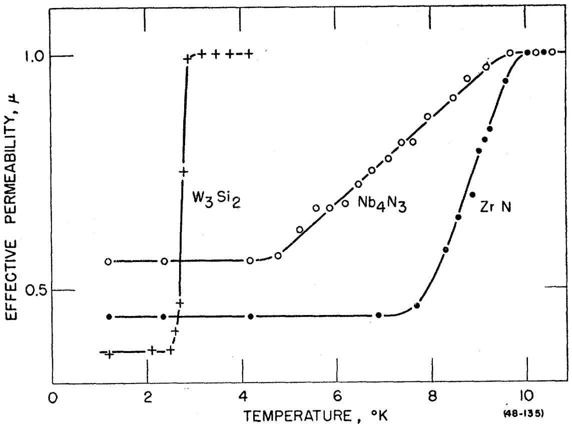

FIG. 5. Temperature variation of effective permeability for sintered ZrN, Nb_4N_3, and W_3Si_2 specimens, measuring field 26 oersteds.

From the temperature of the sudden onset of superconductivity in specimen *A*, extrapolated to zero field, we obtain a value 5.6°K for the transition point of pure TiN. This compares quite favorably with the upper electrical transition observed by Meissner and Franz; their second transition at 1.2°K may have been due to oxygen contamination or perhaps to the presence of impure titanium metal.[36]

Samples of ZrN prepared by the same method as TiN gave quite broad superconducting transitions of the type shown in Fig. 5, with mid-points in all cases close to 8.9°K, in good agreement with Meissner and Franz's electrical data. Oxygen contamination does not seem seriously to affect the superconductivity of this compound, perhaps because the formation of ZrO_2 is preferred to the replacement of nitrogen by oxygen in the nitride lattice; no evidence has been found for the existence of ZrO.[37]

In preparing VN by heating NH_4VO_3 in ammonia, previous investigators [38,39] found that at temperatures high enough to ensure complete reduction of the vanadium oxides (about 1200°C), the VN itself loses appreciable amounts of nitrogen. To see how this affected the superconductivity, we prepared three VN specimens of about the same shape at three different temperatures, with the results shown in Table IV and Fig. 6. Even though specimen *A* contained the most oxygen, it exhibits the sharpest superconducting transition and the lowest effective permeability, probably owing to the fact that the oxygen occurs as

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[34] P. Ehrlich, Z. anorg. u. allgem. Chem. **259**, 1 (1949).

[35] A. K. Brager, Acta Physicochim. U.R.S.S. **11**, 617 (1939).

[36] Although the present accepted transition temperature of titanium is 0.53°K, early specimens had transitions at 1.2° and 1.8°K, presumably owing to impurities. See reference 12, p. 223.

[37] D. D. Cubicciotti, J. Am. Chem. Soc. **73**, 2032 (1951).

[38] V. A. Epelbaum and B. F. Ormont, Acta Physicochim. U.R.S.S. **22**, 319 (1947).

[39] H. Hahn, Z. anorg. u. allgem. Chem. **258**, 58 (1949).

TABLE IV. Influence of preparation temperature on the superconductivity of VN.

Specimen	Prepn. temp. (°C)	Oxygen content (wt. %)	Nitrogen content (wt. %)	Latt. par. (A)	T_c[a] (°K)
A	1000	7.6	13.7	4.135	8.2
B	1200	2.3	18.6	4.132	6.7
C	1350	2.4	11.8	4.130	5.8

[a] Onset temperature extrapolated to zero field.

residual oxides (VO_2 or V_2O_5) which are not superconducting. As the preparation temperature is raised, more oxygen is driven off but at the same time more apparently goes into solution in the VN lattice and depresses the superconducting transition point. This may have been responsible for the low transition temperature observed by Meissner and Franz; in view of the fact that our specimen *A* was the most completely superconducting and gave a lattice parameter closest to the values reported by previous workers[39–41] for pure VN (4.134A and 4.137A), we regard the temperature of onset of superconductivity in this specimen (8.2°K) as the most reliable transition temperature at present available.

In addition to the above mononitrides we tested the seven compounds Th_3N_4, "V_5N_2," Nb_2N, Nb_4N_3, Ta_2N, TaN, and UN down to 1.20°K. Normal behavior was observed in all cases except that of Nb_4N_3, which became superconducting over a range of 5°K with its mid-point at 7.2°K (Fig. 5); according to Brauer and Jander[42] this compound has a crystal structure based upon a tetragonally deformed NbN (NaCl type) lattice. In view of the high transition points of the vanadium and niobium mononitrides, and of the metals themselves, it is interesting that the hexagonal lower nitrides "V_5N_2" and Nb_2N remain normal down to 1.20°K. Both these compounds involve a close-packed hexagonal metal lattice with nitrogen atoms in the interstices[30,39]; however, as Hahn has pointed out, since the holes in the vanadium lattice are too small for the nitrogen atoms, the compound is formed in the range $VN_{0.37}$ to $VN_{0.43}$ instead of at the ideal composition $VN_{0.50}$.

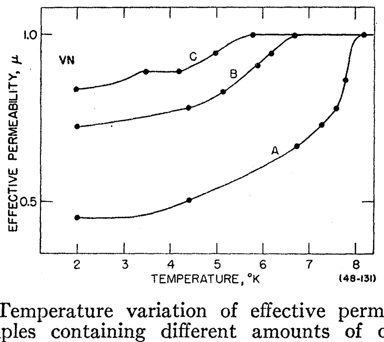

FIG. 6. Temperature variation of effective permeability for "VN" samples containing different amounts of oxygen and nitrogen (Table IV), measuring field 26 oersteds.

The absence of superconductivity in Th_3N_4 is perhaps to be expected, since this compound is usually regarded as a typical "ionic" and nonmetallic nitride.[43] While our particular specimen of TaN showed no trace of superconductivity, its x-ray diffraction pattern did not resemble that reported by Horn and Ziegler[8] for a sample which remained normal down to 1.88°K, and neither of these patterns agree with that given by Becker and Ebert[44] for TaN. On the other hand, our Ta_2N, which was made by heating an intimate mixture of TaN and tantalum at 1450°C, gave a hexagonal pattern similar to that of Nb_2N and identical with the data of van Arkel[45] for a specimen which he called "TaN." Chiotti[46] has shown convincingly that this hexagonal close-packed phase is actually the heminitride of tantalum, but the structures existing around the composition "TaN" remain obscure.

D. Oxides

Arc-melted pellets of the monoxides TiO, VO, and NbO showed no trace of superconductivity down to 1.20°K. The TiO and VO specimens were found to have a sodium chloride structure, with lattice parameters in good agreement with values obtained by earlier workers.[47,48] NbO also gave an x-ray diffraction pattern in good agreement with that previously reported,[49] which apparently corresponds to a structure derived from the NaCl type by the orderly removal of niobium and oxygen atoms from one-fourth of the lattice positions. These oxides all had a metallic appearance; VO and NbO were silvery and TiO was a dull golden color. Rough tests showed that the electrical resistivity of the latter was about 300 micro-ohm cm at room temperature and rose by a few percent on cooling to

TABLE V. Superconducting silicides and germanides of Groups 4, 5, and 6 transition metals (present work).

None found for titanium or zirconium	V_3Si (17.1°) V_3Ge (6.01°)	None found for chromium
None tested for hafnium	["Nb_2Ge" (1.9°)][a]	Mo_3Si (1.30°) Mo_3Ge (1.43°)
α-$ThSi_2$ (3.16°) β-$ThSi_2$ (2.41°)	["Ta_2Ge" (1.6°)][a]	W_3Si_2 (2.84°)

[a] Doubtful owing to presence of free metal.

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[40] A. K. Brager and V. A. Epelbaum, Acta Physicochim. U.R.S.S. **13**, 595 and 600 (1940).

[41] V. A. Epelbaum and B. F. Ormont, Zhur. Fiz. Khim. **21**, 3 (1947).

[42] G. Brauer and J. Jander, Z. anorg. u. allgem. Chem. **270**, 160 (1952).

[43] A. F. Wells, *Structural Inorganic Chemistry* (Oxford University Press, London, 1950) second edition, p. 477.

[44] K. Becker and F. Ebert, Z. Physik **31**, 268 (1925).

[45] A. E. van Arkel, Physica **4**, 286 (1924).

[46] P. Chiotti, J. Am. Ceram. Soc. **35**, 123 (1952).

[47] W. Rostoker, J. Metals **4**, 981 (1952). (Our TiO specimen was obtained from Dr. W. Rostoker.)

[48] W. Klemm and L. Grimm, Z. anorg. u. allgem. Chem. **250**, 42 (1942).

[49] G. Brauer, Z. anorg. u. allgem. Chem. **248**, 1 (1941).

78°K, which suggests semiconducting behavior. It should be remarked that Meissner, Franz, and Westerhoff[6] found a gradual drop in electrical resistance for NbO between about 4.2° and 1.4°K, which, in view of the present results, was probably due to impurities.

E. Silicides

Although the radius of silicon is too large for the extensive formation of interstitial compounds, many of the transition metal silicides have metallic character and their structures have been extensively studied.[50] In the present work all the known silicides of the Groups 4, 5, and 6 transition metals, with the exception of hafnium and uranium, were tested for superconductivity down to 1.20°K. The results of these studies, together with those for similar tests on the corresponding germanides, are summarized in Table V (superconducting) and Table VI (normal).

TABLE VI. Silicides and germanides of Groups 4, 5, and 6 transition metals nonsuperconducting down to 1.20°K (present work).

Ti_5Si_3, Ti_5Ge_3	"V_3Si_2," V−Ge	Cr_3Si, Cr_3Ge
TiSi	VSi_2	Cr_3Si_2, Cr_3Ge_2
$TiSi_2$, $TiGe_2$		CrSi, CrGe
	Nb_3Si_2	$CrSi_2$
Zr_4Si, Zr_2Si	"Nb_2Si"	
Zr_3Si_2, Zr_4Si_3	$NbSi_2$, $NbGe_2$	Mo_3Si_2, Mo_3Ge_2
Zr_6Si_5		$MoSi_2$
ZrSi, Zr−Ge	Ta_5Si, Ta_5Si_2	α-$MoGe_2$
$ZrSi_2$, $ZrGe_2$	Ta_3Si_2	β-$MoGe_2$
	$TaSi_2$, $TaGe_2$	
Th_3Si_2, Th−Ge		WSi_2

Superconducting behavior was observed in the five silicides V_3Si (17.1°K, Fig. 7), Mo_3Si (1.30°K, Fig. 3), α-$ThSi_2$ (3.16°K, Fig. 8), β-$ThSi_2$ (2.41°K, Fig. 8), and W_3Si_2 (2.84°K, Fig. 5), representing four structure types in which the phenomenon has not previously been reported. The most striking feature of these results is the transition temperature of V_3Si, which is the highest known for any binary compound. Since both V_3Si and Mo_3Si crystallize in a cubic structure of the β-tungsten type [O_h^3], it is interesting that a third silicide of the same structure, Cr_3Si, remains normal down to 1.20°K. According to Zener[51] these compounds might be expected to possess an antiferromagnetic spin arrangement, but this point does not seem to have been checked with neutron diffraction; there is at present no known case in which superconductivity and antiferromagnetism coexist.

At an early stage in the investigation of V_3Si it was found that certain impurities often present in commercial vanadium metal, in particular iron, tend to depress the superconducting transition temperature. The transition curves for three specimens prepared from vanadium obtained from three different sources are shown in Fig. 7; Table VII gives the main impurity content of these specimens and indicates that as little as 0.1 percent of iron lowers the transition temperature by nearly one degree. Since all our specimens contained about the same amount of manganese, it was not possible to decide how much effect this impurity had upon the transition temperature. However, since the neighboring elements iron and chromium (see Table VIII) tend to depress the transition, manganese probably has the same effect and we presume that the transition temperature of extremely pure V_3Si lies somewhat above 17°K.

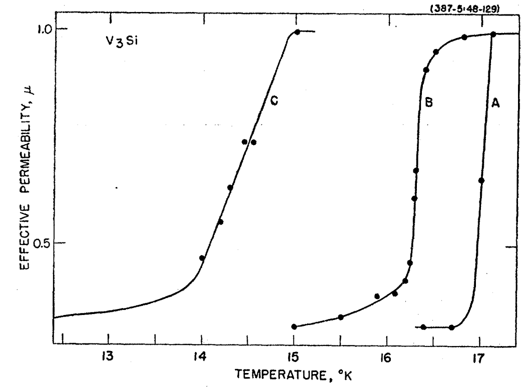

FIG. 7. Temperature variation of effective permeability for arc-melted V_3Si samples containing different amounts of impurity (Table VII), measuring field 8 oersteds.

In an attempt to raise the transition temperature of V_3Si specimens, we investigated the effect of varying the silicon content and also of replacing part of the vanadium or silicon by other elements. Changes up to ±20 atomic percent of silicon produced hardly any change of T_c, probably because the single phase region for V_3Si is rather narrow. The introduction of other elements caused the changes listed in Table VIII; although many of the added elements did not dissolve completely in the V_3Si phase, in spite of melting in the

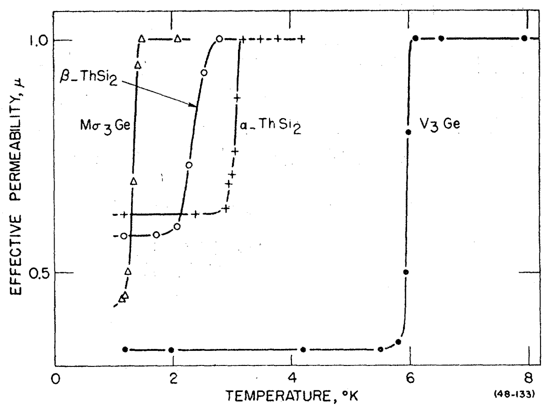

FIG. 8. Temperature variation of effective permeability for arc-melted V_3Ge, Mo_3Ge, and sintered α-$ThSi_2$, β-$ThSi_2$ specimens, measuring field 26 oersteds.

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[50] For a detailed list of papers, see reference 1.

[51] C. Zener, Phys. Rev. 81, 440 (1951).

TABLE VII. Influence of impurities on the superconductivity of V_3Si.

Specimen	Impurities % Fe	% Mn	Latt. par. (A)	Mid-point[a] (°K)
A	0.05	0.2	4.722	17.0
B	0.1	0.3	4.723	16.3
C	1.0	0.3	4.720	14.4

[a] Applied field 8 oersteds.

arc furnace, the results show that the transition temperature was lowered in all cases.

Of the remaining new superconductors, the tetragonal compound α-$ThSi_2$ [D_{4h}^{19}] is well known[52]; we tested the isomorphous compounds[53–55] $CeSi_2$, $LaSi_2$, and YSi_2 (distorted), but all three remained normal down to 1.20°K. A series of Th-Si specimens of different silicon contents also yielded, in addition to α-$ThSi_2$, two previously unreported phases,[56] β-$ThSi_2$ [hexagonal (D_{6h}^{1}) superconducting at 2.41°K] and Th_3Si_2 [tetragonal (D_{4h}^{5}) normal]. These specimens also contained a good deal of ThO_2, which, however, merely served to increase the effective permeability in the superconducting range.

In a previous paper[11] superconductivity was reported in Mo_3Si_2, which is apparently isomorphous with the superconductor W_3Si_2, both structures being unidentified. This result was an erroneous one due to the presence of Mo_3Si impurities in the original "Mo_3Si_2" specimen. Since the x-ray diffraction pattern of pure Mo_3Si_2 contains all the lines of Mo_3Si, the presence of these impurities remained undetected for some time. However, prolonged annealing of the specimen caused the superconductivity to disappear, presumably owing to the removal of Mo_3Si.

It is of interest to mention some normal phases found by us in silicide systems which have hitherto been incompletely explored. For the vanadium-silicon system a new phase of unknown structure was observed at the approximate composition V_3Si_2. In addition to $NbSi_2$, two lower niobium silicides have been previously mentioned without x-ray diffraction data.[57] Our specimens sintered at 1450°C contained a phase of approximate composition Nb_5Si_3; we found the x-ray diffraction pattern to be identical with that reported[58] for Ta_5Si_3. Arc-melted specimens gave an additional phase of composition Nb_2Si which is apparently formed only at very high temperatures.

Finally, we note that four tantalum silicides[58,59] remained normal down to 1.20°K, which strongly suggests that the disappearance of electrical resistance observed by Meissner, Franz, and Westerhoff[7] in a "TaSi" specimen was due to impurities, probably free tantalum.

F. Germanides

Structural interest in the transition metal germanides is quite recent, and far less information is available than for the silicides. However, the data so far obtained seem to indicate that the silicides and germanides of a given transition metal are much more closely related to each other than to the carbides or nitrides of that metal. Whereas the carbides and nitrides tend to have "interstitial" structures, the silicides and germanides have structures based, to some extent, on bonding of nonmetal atoms to each other,[53] and on equivalence between the roles of metal and nonmetal atoms in the structure, in analogy with the borides.[24]

We tested the known germanides of the Groups 4, 5, and 6 metals down to 1.20°K, with the results given in Tables V (superconducting) and VI (normal). Only two new superconductors were observed, V_3Ge (6.01°K, Fig. 8) and Mo_3Ge (1.43°K, Fig. 8), both of which are isomorphous with V_3Si.[60,61]

In view of our incomplete knowledge of the phase diagrams, it was usual to prepare for each transition metal about eight sintered specimens of different germanium contents in the range M_4Ge to MGe_2, where M is the metal. X-ray studies for the systems Zr-Ge, Th-Ge, and V-Ge indicated the presence of several new phases in addition to the known compounds[60] $ZrGe_2$ and V_3Ge, but since none of these were superconducting above 1.20°K, they were not investigated further. In both arc-melted and sintered specimens of Nb-Ge and Ta-Ge, evidence was found for existence of

TABLE VIII. Effect of added elements on the superconductivity of V_3Si.

Composition	Latt. par. (A)	Trans. range[a] (°K)	Mid-point[a] (°K)
V_3Si	4.722	16.4–17.1	16.8
$V_3Si_{0.9}C_{0.1}$	4.723	15.5–16.7	16.4
$V_2Si_{0.9}Ge_{0.1}$	4.731	13.0–14.4	14.0
$V_3Si_{0.9}B_{0.1}$	4.720	15.0–16.3	15.8
$V_3Si_{0.9}Al_{0.1}$	4.727	13.1–14.9	14.05
$(V_{0.9}Ti_{0.1})_3Si$	4.736	10.0–12.0	10.9
$(V_{0.9}Zr_{0.1})_3Si$	4.724	11.0–15.3	13.2
$(V_{0.9}Nb_{0.1})_3Si$	4.756	12.0–13.5	12.8
$(V_{0.9}Mo_{0.1})_3Si$	4.732	11.5–12.5	11.7
$(V_{0.9}Cr_{0.1})_3Si$	4.697	11.0–11.9	11.3
$(V_{0.9}Ru_{0.1})_3Si$	4.707	2.0– 3.8	2.9

[a] Applied field 26 oersteds.

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[52] G. Brauer and A. Mitius, Z. anorg. u. allgem. Chem. **249**, 325 (1942).

[53] W. H. Zachariasen, Acta Cryst. **2**, 94 (1949).

[54] F. Bertaut and P. Blum, Acta Cryst. **3**, 319 (1950).

[55] G. Brauer and H. Haag, Z. anorg. u. allgem. Chem. **267**, 198 (1952).

[56] We are indebted to Professor W. H. Zachariasen for informing us of his unpublished structural results for these two phases (to be published shortly) and for identifying the phases in our specimens.

[57] G. Brauer, in W. Klemm, *FIAT Review of German Science 1939–1946, Inorganic Chemistry*, Part II (1948), p. 105.

[58] Brewer, Searcy, Templeton, and Dauben, J. Am. Ceram. Soc. **33**, 291 (1950).

[59] Nowotny, Schachner, Kieffer, and Benesovsky, Monatsh. Chem. **84**, 1 (1953).

[60] H. J. Wallbaum, Naturwiss, **32**, 76 (1944).

[61] Searcy, Peavler, and Yearian, J. Am. Chem. Soc. **74**, 566 (1952).

the previously reported[60] digermanides, which remained normal down to 1.20°K, and two lower compounds of approximate composition "Nb_2Ge" and "Ta_2Ge" which showed superconducting behavior at about 1.9° and 1.6°K, respectively. However, since free metal was present in all specimens of these hemigermanides, their superconductivity remains in doubt.

In the Ti-Ge, Cr-Ge, and Mo-Ge specimens, only known compounds were present,[60–62] the normal compounds including Mo_3Ge_2 and two forms of $MoGe_2$ upon which x-ray data has recently been published.[63] Just as for Mo_3Si_2, discussed in Sec. III E, the superconducting behavior previously reported[11] for Mo_3Ge_2 disappeared after prolonged annealing and was therefore presumed to have been due to Mo_3Ge impurities. No compounds were found in the W-Ge system.

G. Other Compounds

Since superconductivity was observed in four compounds, V_3Si, V_3Ge, Mo_3Si, and Mo_3Ge, which crystallize in a structure of the β-tungsten type, it was thought worth while to test several intermetallic compounds of this structure. However, four such compounds, Ti_3Pt,[64] Ti_3Au,[64] V_3Co,[65] and Mo_3Zr,[66] remained normal down to 1.20°K.

The lowest known sulphide of niobium, NbS,[67] was prepared by heating the powdered metal and sulphur in a sealed, evacuated "Vycor" tube at about 1000°C until equilibrium was attained. No trace of superconductivity was observed in this compound down to 1.28°K.

IV. CONCLUSION

Excluding the bismuthides,[9] about thirty compounds of metals with nonmetallic elements have now been shown to be superconducting on the basis of quite reliable magnetic evidence. Most of these are listed in Tables I and V, including the eleven new superconductors found in the present work; the others comprise CuS [68] and several compounds of Group 8 metals recently reported superconducting by Matthias.[69] Errors in early work due to reliance upon electrical measurements or due to inadequate knowledge of the specimen composition have now been largely corrected. Most of the compounds of Groups 4, 5, and 6 transition metals with boron, carbon, nitrogen, oxygen, silicon, and germanium have been tested for superconductivity down to about 1°K, but even here, as the detailed phase diagrams (which are lacking in most cases) become available, a few new compounds will probably remain to be tested. Attention should be drawn to the fact that the fraction of superconducting compounds in our tables is roughly the same as the fraction of known superconducting elements, that is, about one-fourth of the total.

The superconducting compounds now outnumber the superconducting elements (21), and offer a greater diversity of structures than heretofore. The most common structure for such compounds is still the cubic NaCl type (5 normal, NbC, NbN, TiN, ZrN, VN, and 3 distorted, Nb_4N_3, Mo_2N, W_2N), but the cubic β-tungsten type (V_3Si, V_3Ge, Mo_3Si, and Mo_3Ge) and the hexagonal structure based upon a close-packed array of metal atoms with nonmetal atoms in the interstices (Nb_2C, Ta_2C, Mo_2C, W_2C, and very distorted NbB) have recently come into prominence. There are also at least ten other important superconducting structure types, ranging in symmetry from the cubic fluorite type[70] ($CoSi_2$) through the tetragonal $CuAl_2$ type (the hemiborides), the tetragonal α-$ThSi_2$ type, the hexagonal NiAs type[69] to the orthorhombic MnP and monoclinic PdBi types.[69] There are several unknown structures, including for example W_3Si_2; this compound is probably closely related to its cubic neighbor Mo_3Si.

It was remarked in a previous paper[9] that superconducting transition temperatures of both cubic elements and compounds tend to be higher than those for hexagonal elements and compounds. This tendency seems to have been confirmed in the present work, in view of the rather high transition points of the β-tungsten structure vanadium compounds and the cubic mononitrides, in contrast to the absence of superconductivity in the hexagonal heminitrides and the low transition points of the hexagonal hemicarbides. It must be admitted, however, that the normal behavior of most of the cubic monocarbides forms an exception to the above hypothesis.

As regards the positions of the superconducting compounds in the periodic system, if one excludes the thorium disilicides, Tables I and V seem to indicate a diagonal character in the arrangement, that is, a displacement to the right (higher group number) as one proceeds down a column of the table. This is due to the persistent failure of either hafnium or chromium to form superconducting compounds; the fact that fourteen chromium compounds remain normal down to 1.28°K may be partly due to the magnetic influence of the incomplete chromium d shell. One may contrast with this the extensive formation of superconducting compounds by the other Group 6A metals, molybdenum and tungsten, which apparently come close to possessing the requisite electronic structure for superconductivity.

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Recently certain theoretical relationships have been established[71,72] between the occurrence of superconductivity in a metal and the normal properties of the metal, in particular the "ideal" electrical resistivity at room temperature. While in their present form these relations seem to be mainly applicable to metals of rather simple outer electronic structure, nevertheless it would be interesting to test their validity for a few of the approximately one hundred compounds listed in our tables. In particular, the added complication of differences of crystal structure, which are not taken into account in the above free-electron theories, might be removed by working with an isostructural group such as the NaCl structure monocarbides, mononitrides, and monoxides with many superconducting and normal members. Unfortunately, however, little accurate information is available on the normal properties of most of these compounds, chiefly owing to the difficulty of preparing them in stoichiometric, homogeneous, solid form. Various estimates[1] of the room-temperature electrical resistivities of the carbides and nitrides, for example, differ by more than an order of magnitude in some cases, and since hardly any low-temperature data are available, it is impossible to derive accurate values of the "ideal" resistivity. If the most recently obtained resistivity values are assumed to be correct, the nitrides, which include most of the superconductors of NaCl structure, seem to have resistivities predominantly lower than those of the carbides and monoxides, but beyond this little can be said.

A more systematic investigation of the normal electronic properties of transition metal compounds is clearly desirable, not only for the light which may be thrown on their superconducting behavior, but also for the intrinsic interest of the chemical binding in these compounds. Whereas many are known to have metallic character, a few semiconductors, such as titanium monoxide, have also been reported; thus, solid solutions of TiC or TiN with TiO may provide a continuous transition from metallic to semiconducting properties in the same, relatively simple lattice. A similar, but less smooth, transition may occur with increasing nonmetal content in the borides and silicides, since during this increase each boron or silicon atom tends to form step by step a greater number of linkages with its boron or silicon neighbors. Experiments to check these hypotheses through the detailed study of electrical properties are now in progress.

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