A Search for New Superconducting Compounds

B. T. MATTHIAS* AND J. K. HULM

Institute for the Study of Metals, University of Chicago, Chicago, Illinois

(Received May 12, 1952)

In an effort to throw new light on the electronic and structural conditions necessary for superconducting behavior, a magnetic test for superconductivity was applied to about ninety binary and ternary compounds at temperatures down to 1.28°K. The new superconductors Mo_2N, MoN, Mo_2B, NbB, $SrBi_3$, and $BaBi_3$ were discovered, and the superconductivity of TiN, ZrN, VN, Mo_2C, MoC, and W_2C, reported by previous investigators using the inconclusive electrical resistance test, was confirmed magnetically. No trace of superconductivity was observed in any one of the several ionic, covalent, or semiconducting compounds examined or in nine borides with boron content greater than 50 atomic percent. The results are discussed in relation to crystal structure and the periodic table.

I. INTRODUCTION

THE study of superconducting compounds began over twenty years ago when, following the discovery at Leiden and at Toronto that superconductivity occurs in many alloys and intermetallic compounds as well as in pure metals, Meissner and his co-workers[1-4] found that certain compounds of metals with nonmetallic elements such as nitrogen, carbon, and sulphur also become superconducting at solid hydrogen or liquid helium temperatures. One of the most interesting results disclosed by this work was that in some compounds, such as CuS, superconducting behavior was induced by the introduction of the nonmetal, since by itself the metallic element was known to remain normal down to the lowest temperatures of measurement. Although he tested quite a large number of binary compounds for superconductivity, Meissner unfortunately employed the electrical resistance method of measurement, which has since been shown to give ambiguous results in the case of impure specimens.[5] More recently a number of compounds have been tested by Justi and his co-workers[6] and by Horn and Ziegler,[7] while in the related field of intermetallic compounds of nonsuperconducting elements the early work of de Haas, von Aubel, and Voogd[8] on gold-bismuth has been extended by Alekseyevsky[9,10] and Reynolds and Lane.[11] The situation has remained far from satisfactory, however, in view of the large number of interesting compounds that have not been examined at low tempera-

tures and owing to uncertainties regarding the extent to which the early experiments were affected by impurities and by deviations from stoichiometric composition. These difficulties led us some time ago to commence a new experimental survey of intermetallic and semimetallic compounds, the object being to remove some of the ambiguities of the earlier work and if possible to throw new light on the chemical and structural conditions governing the occurrence of superconductivity. While it seems unlikely that these conditions will be throughly understood until the quite well-established magnetic, electrical, and thermal properties of an "ideal" superconductor receive a satisfactory fundamental explanation, nevertheless, it is probable that both the chemical and physical objectives would be brought somewhat nearer if one knew the full range of types of solid and crystal lattices in which superconductivity is possible. Although our experiments have so far by no means completely answered the latter question, the results for about ninety compounds indicate certain solid types as unfavorable to superconductivity and also give a number of new superconductors which seem to be worth describing at the present time. Under the latter heading we shall discuss superconducting compounds of boron, carbon, and nitrogen with certain transition metals, some of which have already been briefly described,[12] and also some new intermetallic compounds of bismuth.

II. EXPERIMENTAL DETAILS

A. Method

The determination of superconducting behavior through the disappearance of the electrical resistance of a specimen suffers from the disadvantage that a small filament of superconducting impurity may short-circuit the bulk of the specimen and produce a large but spurious effect.[5,13,14] This difficulty may be to some

* Now at Bell Telephone Laboratories, Murray Hill, New Jersey.
[1] W. Meissner, Z. Physik 58, 570 (1930).
[2] W. Meissner and H. Franz, Z. Physik 65, 30 (1930).
[3] Meissner, Franz, and Westerhoff, Z. Physik 75, 521 (1932).
[4] W. Meissner, Wien-Harms Handbuch der Exp. Physik 11, 2 (Akad. Verlagsgesellschaft m.b.H., Leipzig, 1935).
[5] D. Shoenberg, Nature 159, 303 (1947).
[6] Aschermann, Friederich, Justi, and Kramer, Physik. Z. 42, 349 (1941).
[7] F. H. Horn and W. T. Ziegler, J. Am. Chem. Soc. 69, 2762 (1947).
[8] de Haas, van Aubel, and Voogd, Leiden Comm. No. 197a and 197c (1929).
[9] N. Alekseyevsky, J. Phys. (U.S.S.R.) 9, 350 (1945).
[10] N. Alekseyevsky, J. Exptl. Theor. Phys. 18, 101 (1948); 19, 671 (1949) and 20, 863 (1950).
[11] J. M. Reynolds and C. T. Lane, Phys. Rev. 79, 405 (1950).

[12] J. K. Hulm and B. T. Matthias, Phys. Rev. 82, 273 (1951).
[13] This appears to have been the case, for example, in some of the early work on carbides. Ziegler and Young (see reference 14) recently found that certain carbides exhibit normal magnetic behavior in temperature ranges where superconducting resistance transitions had previously been reported by Meissner and Franz (see reference 2 and Sec. III D). Electrical resistance data must

extent overcome by measuring the change in magnetic induction of the specimen due to a given change in a small, externally applied magnetic field, or, in other words, determining the initial permeability of the specimen. Since a small, applied magnetic field cannot produce an appreciable induced field at a depth greater than about 10^{-5} cm, the penetration depth, below the surface of a homogeneous superconducting body, the initial permeability of such a body with linear dimensions large compared to 10^{-5} cm is essentially zero. The extent to which the permeability of an inhomogeneous
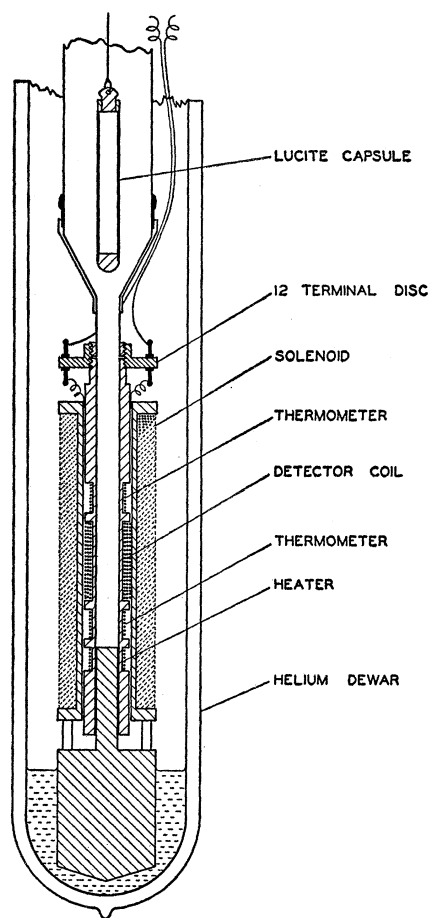

FIG. 1. Magnetic permeability apparatus.

specimen containing some superconducting regions differs from zero may give a rough idea of the volume of flux-linkable space or normal matter present, and with the aid of x-ray and chemical analysis the superconducting phase can often be identified unambiguously, in spite of the presence of considerable impurity. This is certainly possible for solid, superconducting grains

undoubtedly be treated with caution, and we hope to check magnetically all the important earlier results based solely on resistance measurements.

[14] W. T. Ziegler and R. A. Young, Report of the International Low Temperature Conference, Oxford, England, August, 1951.

in a normal matrix, but presents difficulties for normal grains in a superconducting matrix, since isolated normal regions may be completely screened from the applied field and contribute nothing to the total induction. That is to say, the effective permeability may differ appreciably from unity in spite of the presence of a relatively small volume of superconducting material, providing that this material is distributed in a "sponge-like" structure so as to sheath a large amount of normal material to a depth greater than the penetration depth. Such behavior has, in fact, been reported by Hudson[15] for tin-germanium alloys and has been experienced for certain compounds studied in the present work, as will be mentioned in the detailed discussion of experimental results. For the time being it will be remarked that although a consideration of impurities is important in the magnetic test as well as in the electrical test for superconductivity, in practice the permeability seems to be less sensitive to impurities than the resistance, presumably because closed superconducting sheaths are formed less readily than superconducting filaments. The magnetic method has the additional advantage that it is applicable to any state of physical aggregation, whereas solid rods, which are often difficult to fabricate, are necessary for satisfactory resistance measurements.

B. Magnetic Apparatus

Our particular system was designed to allow rapid testing of a fairly large number of specimens. Each sample, either in the form of a solid rod, or as a powder packed into a thin-walled cylindrical Lucite capsule, or sealed within a glass tube containing an atmosphere of helium gas in the case of materials unstable in air, was attached to the end of a Nylon fishing line and lowered into the arrangement shown schematically in Fig. 1. The sample was guided by a metal funnel into an 8-mm diameter Lucite tube on the outside of which was wound a detector coil, a heater coil, and two resistance thermometers. The detector coil consisted of 1000 turns of 40-gauge Formex-insulated copper wire wound in 3 layers on the Lucite tube, and changes in the induction of the specimen could be measured by observing the throw of a critically damped, high sensitivity galvanometer connected in series with the coil. In order to minimize the flux that leaked between the coil winding and the specimen material, the gap between these, including both Lucite and clearance space, was rarely allowed to exceed 0.07 mm. A magnetic field of a few oersteds could be applied to the specimen by a small solenoid which fitted closely around the specimen and detector coil. The whole arrangement was located in a liquid helium Dewar flask which was in turn surrounded by a liquid nitrogen flask and formed part of a conventional helium cryostat not shown in Fig. 1.

[15] R. P. Hudson, Phys. Rev. 79, 883 (1950).

C. Measuring Technique

For measurements below 4.2°K the detector system was completely immersed in liquid helium, and temperatures down to 1.28°K could be attained using a 45-liters-per-second pump suitably connected to the cryostat. Temperatures were obtained from the vapor pressure of the helium bath, using the 1949 International Scale.[16] Any one of six specimens could be lowered into the detector coil at a given temperature by means of six winches situated in the helium gas at the top of the cryostat. The winches were operated from the outside by driving rods packed with Teflon and were observed through a clear Lucite plate sealed into the top of the cryostat. To facilitate testing of more than six specimens down to 1.28°K, the entire winch assembly could easily be removed and new specimens quickly attached to the Nylon lines. The whole procedure of admitting helium gas to the cryostat to increase the pressure up to atmospheric value, changing specimens, and pumping down to 1.28°K again could be accomplished in a few minutes and with the loss of only a small quantity of liquid helium, probably because the main bulk of the bath did not have time to warm above the lambda-temperature. In this manner as many as 24 specimens were dealt with for one shot of liquid helium in the cryostat.

For measurements above 4.2°K the liquid helium level was allowed to fall below the detector coil and manganin heater coil, as shown in Fig. 1, whereupon the specimen temperature could be raised slowly by regulating the pumping speed and heater current. Temperatures were measured by two 1000-ohm, noninductive, constantan resistance thermometers which had a sensitivity of about 1 ohm per degree and which were located one above and one below the detector coil. These thermometers were calibrated in the liquid hydrogen and liquid helium ranges, and temperatures in the in-
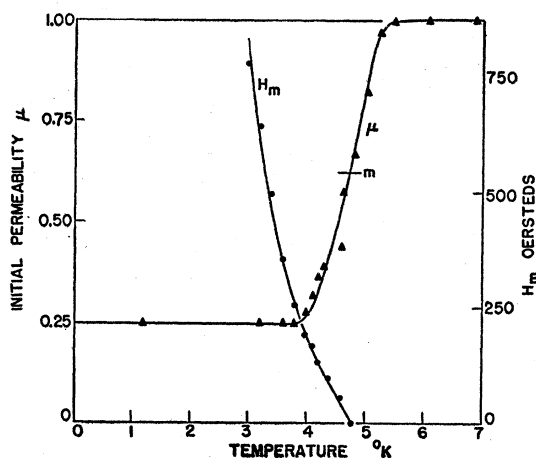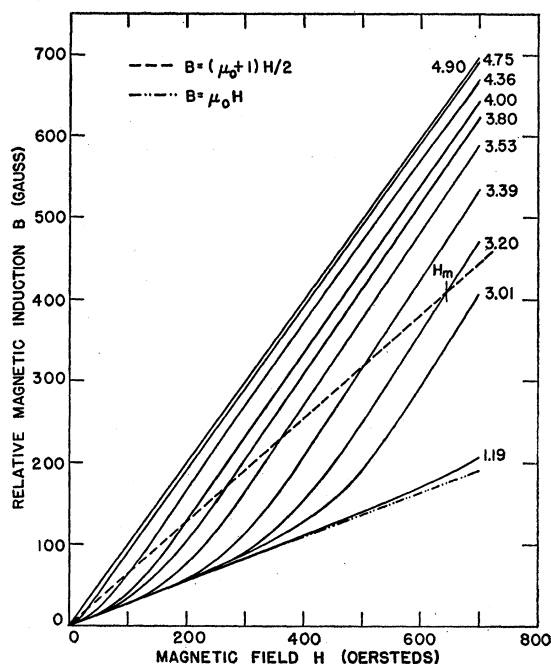

FIG. 3. Magnetic induction—magnetic field curves at various temperatures, Mo₂B specimen.

termediate range were obtained by interpolation. Since a difference of a few tenths of a degree usually existed between the two thermometers in the 4.2° to 10°K range, specimen temperatures in this range were known to little better than 0.5°K.

The usual procedure was to observe the galvanometer throw produced by switching off a field of about 10 oersteds, which is considerably less than the limiting critical field for most superconductors with transition temperatures above 1°K. During the "on" period the solenoid current was stabilized with a potentiometer circuit, so that by measuring the galvanometer throw for unit permeability before lowering the specimen into the coil, initial permeabilities close to unity could be determined with about 0.2 percent absolute accuracy and traces of superconducting behavior could readily be observed. The variation of permeability with temperature for most of the superconducting powder samples was of the type shown in Fig. 2, with the transition spread out over an appreciable range. The transition temperature was estimated in such cases from the midpoint m corresponding to a permeability of $(\mu_0+1)/2$, where $\mu\rightarrow\mu_0$ as $T\rightarrow0$.

The initial permeability data were supplemented in a few cases by measurements at various temperatures of magnetic induction—magnetic field curves for field strengths up to 700 oersteds, using a large, external solenoid. These magnetic field transitions were also of the spread-out type shown in Fig. 3, where the term "relative magnetic induction" denotes the fact that all induction values were referred to the same zero, ignoring the contribution of frozen-in flux. Measurements

FIG. 2. Temperature variation of initial permeability μ and midpoint field H_m for Mo₂B specimen.

[16] H. van Dijk and D. Shoenberg, Nature 164, 151 (1949).

based on the virgin magnetic state showed the latter contribution to be quite large in some cases. Defining the field H_m (not to be confused with the critical field H_c) as the field at which B attains a value $(\mu_0+1)H_m/2$, one may expect the curve of H_m versus T to intersect the temperature axis at the temperature of the midpoint m of the initial permeability curve. Since this was found to be true for several typical specimens (e.g., Fig. 2), we frequently used the H_m data alone to estimate the transition temperature. It should be mentioned that H_m was occasionally a linear function of T^2 over quite a wide temperature range, indicating a simple proportionality to H_c.

D. Preparations and Analyses

Most of the specimens were either readily available or could be prepared by methods similar to those described by previous investigators, which need not be discussed in detail. To mention a few essential points, the compounds $SrBi_3$ and $BaBi_3$, of which only the latter had been previously described,[17] were prepared by heating the appropriate mixtures in a controlled helium atmosphere at about 650°C. Both compounds formed as bright, silvery cubes which, however, were rapidly attacked by moist air at room temperature. For superconducting tests the crystals were packed tightly into thin-walled glass tubes which were filled with helium gas at atmospheric pressure before sealing off.

Several of the group 6A nitride specimens were prepared by passing ammonia gas over the heated metal, but in the case of molybdenum and tungsten a much faster reaction was obtained by ammoniating the metallic oxides at about 700°C, a method that does not seem to have been previously reported. Attempts to prepare WN by this method were unsuccessful, no samples being obtained with a nitrogen content appreciably greater than that of W_2N.

Most of the remaining intermetallic compounds and the borides and carbides were prepared using a vacuum induction furnace in which temperatures up to about

TABLE I. Compounds of borderline elements and semiconducting compounds nonsuperconducting down to 1.28°K (present work).

Copper	CuP, $CuSi$, Cu_3As,[a] Cu_2Sb, $CuBr_2$, Cu_2Mg, $CuMg_2$, $CuSe$,[a, b] Cu_2O,[c] CuO[c, d]
Silver	Ag_2O, Ag_2S,[c, d] Ag_2Se,[c] Ag_2Te,[c] Ag_2Be, Ag_2Bi, $AgMg$
Antimony	SbS_3, SbK, Sb_2Cr, Sb_3Ce, $SbBi$, $SbCuMg$
Oxides	MoO_2,[a] UO_2,[c] CoO,[c] NiO,[c] Mn_2O_3, V_2O_3, Tl_2O_3,[a] Rh_2O_3
Sulphides	MoS_2,[c] PbS,[a, c] SnS, CeS, Ce_3S_4, NiS
Others	MoP, SiC,[c] $SiFe$, $PbTe$,[a, c] $NiAs$[a]

[a] Previously tested by Meissner, Franz, and Westerhoff [Ann. Physik 17, 593 (1933)] down to 1.3°K.
[b] Isomorphous with CuS [International Union of Crystallography, Structure Reports, II. N. V. A. Dosthoeks Uitgevers MIJ Utrecht (1951)].
[c] Known semiconductors [F. Seitz, Modern Theory of Solids (McGraw-Hill Book Company, Inc., New York, 1940)].
[d] Previously tested by McLennan, Allen, and Wilhelm [Phil. Mag. 10, 500 (1930)] down to 1.9°K.

[17] E. Grube and A. Dietrich, Z. Elektrochem. 44, 755 (1938).

2100°C could easily be obtained. In recent work some of the more refractory compounds were prepared by melting the appropriate mixtures in a helium arc furnace.

X-ray powder diffraction patterns were taken in all cases where the structure or composition of a specimen were in doubt, while spectrographic analyses were performed for a few samples where the source of a trace of superconducting behavior could not be identified from the other information available. Where structural data are discussed without explicit reference to original papers,[18] the information was obtained from Wyckoff's tables.[18]

Attention may be drawn to one case in which the x-ray results were of special interest, namely, molybdenum carbide, which was prepared in the arc furnace. Our pattern was in good agreement with the γ-phase pattern of Sykes, Kent, and Tucker,[19] except for a slight increase of all interplanar spacings. The latter effect appears to have been due to the fact that about 52 atomic percent of carbon was deliberately employed in our specimen to suppress the β-phase, Mo_2C, whereas the γ-phase studied by Sykes et al. probably contained only 50 atomic percent of carbon. Our x-ray data for MoC show no evidence for the presence of Mo_2C and strengthen the view that the structure of the γ-phase is more complex than the hexagonal arrangement (isomorphous with WC) suggested by Tutiya.[20]

III. RESULTS AND DISCUSSION

A. Compounds of Borderline Elements

It is well known that the twenty-one superconducting elements lie in two distinct regions of the periodic system, within groups 3A to 8A and groups 2B to 4B, respectively, and also that the known superconducting compounds, such as CuS and MoC, formed entirely from nonsuperconducting elements, contain at least one component lying immediately next to one of these two superconducting regions. On the hypothesis that the latter phenomenon springs partially from the fact that such "borderline" elements require the least drastic modification of their electronic character to produce superconducting behavior, we tested several compounds containing one or occasionally two of these elements. Although a large number of the compounds of Table I contain borderline elements in the superconducting sense, and in some cases show pronounced metallic character, they gave no evidence of superconducting behavior down to 1.28°K.

B. Semiconducting Compounds

It is difficult to say with certainty from the available data that a substance which has a resistance-tempera-

[18] R. W. G. Wyckoff, Crystal Structures (Interscience Publishers, New York, 1951), Vol. I.
[19] Sykes, Kent, and Tucker, Trans. Am. Inst. Mining Met. Engrs. 117, 173 (1935).
[20] H. Tutiya, Bull. Inst. Phys. Chem. Research (Tokyo) 11, 121 (1932).

ture curve of the type characterizing semiconduction[21] cannot undergo a superconducting transition at sufficiently low temperatures. This seems likely, of course, on any free-electron theories such as those proposed recently by Fröhlich[22] and Bardeen,[23] and we certainly found no evidence of superconducting behavior in the dozen or so semiconducting compounds listed in Table I. In the case of PbS and PbTe we support the recent conclusions of Hudson[24] that these compounds show normal magnetic behavior at liquid helium temperatures, so that the electrical resistance transition in the neighborhood of 4°K reported for PbS, PbSe, and PbTe by Darby, Hatton, and Rollin[25] was very probably due to filamentous superconducting impurities. Since the experiments of Meissner and his co-workers[4] and the present authors provide negative results for a fairly typical group of ionic and covalent substances, it seems likely at present that metallic bonding is an essential prerequisite for superconducting behavior.

C. Bismuth Compounds

Although bismuth correctly belongs to the class of borderline elements to which reference has already been made, its compounds offer such a markedly different picture from those of other members of the class that it seems best to discuss them separately. Despite the fact that bismuth itself behaves normally down to 0.05°K,[26] it combines with nine other nonsuperconducting metals to form ten distinct superconducting compounds. The available data on these compounds, including results of the present work, are given in Table II.

In view of Alekseyevsky's discovery that $CaBi_3$ becomes superconducting at about 1.7°K, it seemed worthwhile to investigate other compounds of bismuth with alkaline earth metals. We observed superconducting behavior in $SrBi_3$ and $BaBi_3$, obtaining isothermal magnetic field transitions which were of the gradual type described in Sec. II C. Since the half-value field H_m was a linear function of T^2 for both compounds over the whole superconducting range, the results may be expressed in the form

$$SrBi_3, \quad H_m = 530 \ (1 - T^2/31.6) \text{ oersteds,}$$

$$BaBi_3, \quad H_m = 740 \ (1 - T^2/32.4) \text{ oersteds.}$$

The transition temperatures 5.62°K ($SrBi_3$) and 5.69°K ($BaBi_3$), which are the highest ones known for bismuth compounds, replace slightly different, earlier

TABLE II. Superconducting and nonsuperconducting compounds of bismuth with normal metals, including results of previous work (see references). Transition temperature or lowest temperature of measurement in parenthesis.

Superconducting		
LiBi (2.47°)[a]	$CaBi_3$ (1.7°)[b]	Au_2Bi (1.8°)[d]
NaBi (2.22°)[b]	$SrBi_3$ (5.62°)	$RhBi_2$ (2.2°)[b]
KBi_2 (3.6°)[c]	$BaBi_3$ (5.69°)	$RhBi_4$ (2.75°)[b]
		$NiBi_3$ (3.6°)[b]

Nonsuperconducting				
CeBi,	MoBi,	SbBi,	$CeBi_2$,	$GeBi_2$ ⎫
Ag−Bi,	CuMgBi,	Mg_3Bi_2,	MnBi	⎭ (1.28°)

PtBi₃ (1.8°),[b] CrBi₂ (1.57°),[b] Se₃Bi₂, (1.3°),[e] Te₃Bi₂ (1.3°)[e].

[a] L. Guttman and J. W. Stout, Proceedings of the Low Temperature Conference, National Bureau of Standards, March (1951).
[b] See reference 10.
[c] See reference 11.
[d] See reference 8.
[e] Meissner, Franz and Westerhoff, Ann. Physik 17, 593 (1933).

values[27] derived from initial permeability-temperature curves.

Its position in the periodic system and conformity to the $(8-N)$ coordination rule[28] indicates that bismuth lies in the border region between metallic and nonmetallic behavior. Its electrical and magnetic properties[29] point to a nearly filled Brillouin zone and to a conduction electron-to-atom ratio considerably less than one, so that in the formation of superconducting compounds of bismuth the function of the other metal may be mainly to increase the effective number of conduction electrons per atom. From another point of view, Meissner[4] suggested that the superconducting behavior of Au_2Bi and certain lead-bismuth alloys springs from the cubic coordination of bismuth in these solids. Examining this idea in the light of recent evidence, we note that of the six superconducting bismuthides for which structural data are available,[18,30] four (Au_2Bi, KBi_2, $SrBi_3$ and $BaBi_3$) are cubic and two ($LiBi$, $NaBi$) are body-centered tetragonal. Against this, the four nonsuperconductors of known symmetry are the two cubic compounds, CeBi and CuMgBi, and the two hexagonal compounds, MnBi and Mg_3Bi_2. The paramagnetic influence of cerium may inhibit superconductivity in the first case, but if the cubic structure hypothesis is correct, there seems to be no obvious explanation for the normal behavior of CuMgBi. It is also difficult to understand why, despite the close chemical resemblance between antimony and bismuth, none of the compounds formed by antimony and other nonsuperconducting elements are known to exhibit superconducting behavior in the liquid helium range,

[21] W. Shockley, Electrons and Holes in Semiconductors (D. Van Nostrand Company, Inc., New York, 1950).
[22] H. Fröhlich, Phys. Rev. 79, 845 (1950).
[23] J. Bardeen, Phys. Rev. 80, 567 (1950).
[24] R. P. Hudson, Proceedings of the Low Temperature Conference, National Bureau of Standards, Washington, March (1951).
[25] Darby, Hatton, and Rollin, Proc. Phys. Soc. (London) 63, 1181 (1950).
[26] N. Kurti and F. Simon, Proc. Roy. Soc. (London) A151, 610 (1935).

[27] B. T. Matthias and J. K. Hulm, Proceedings of the Low Temperature Conference, National Bureau of Standards, March (1951).
[28] W. Hume-Rothery, The Structure of Metals and Alloys (Institute of Metals, London, 1936).
[29] N. F. Mott and H. Jones, The Theory of the Properties of Metals and Alloys (Oxford Press, London, 1936).
[30] M. Hansen, Der Aufbau der Zweistofflegierungen (J. Springer, Berlin, 1936).

TABLE III. Superconducting nitrides, carbides, and borides, including compounds (denoted *) for which earlier resistance data have been checked magnetically.

TiN (4.86°)[a, b, *]	Mo$_2$N (5.0°)	Mo$_2$C (2.78°)[a, *]
ZrN (9.05°)[a, b, *]	MoN (12.0°)	W$_2$C (2.74°)[d, *]
VN (7.5°)[a, b, *]	MoC (9.26°)[a, *]	Mo$_2$B (4.74°)
NbN (14.7°)[b, c]	NbC (10.3°)[a]	NbB (8.25°)

[a] See reference 2.
[b] See reference 34.
[c] See reference 7.
[d] See reference 38.

although six of these compounds were tested in the present work (Table I) and five by Alekseyevsky.[10]

D. Interstitial Compounds of the Transition Metals

Most of the transition metals form compounds of the type Me_2X, MeX, or MeX_2 or slightly more complex formulas in which the arrangement of the metal atoms Me approximates a face-centered cubic or hexagonal close-packed lattice with the small "metalloid" atoms, X, either hydrogen, boron, carbon, nitrogen, or oxygen in the interstices of the lattice. The structures of many of these compounds have been investigated by Hägg[31] and Kiessling,[32] while Moers[33] found that in several cases the electrical resistivity is similar both in magnitude and temperature variation to that of a typical moderately pure metal. A review of the experiments of Meissner,[4] Ziegler and Young,[14] and the present authors indicates that reliable evidence of superconducting behavior now exists for the nitrides, carbides, and borides listed in Table III.

On the other hand, we observed that the nitrides, carbides, and borides listed in Table IV behave normally down to 1.28°K. Oxides and hydrides will be omitted from the present discussion, since hardly any progress has been made in studying superconductivity in these compounds.

Nitrides

The superconducting behavior of the NaCl-structure mononitrides TiN, ZrN, VN, and NbN was confirmed[34] and a new mononitride, hexagonal MoN, was found to

TABLE IV. Nitrides, carbides, and borides nonsuperconducting down to 1.28°K (present work only).

Group 5A	Nb$_3$B$_4$, NbB$_2$, TaB, Ta$_3$B$_4$, TaB$_2$.
Group 6A	CrN, Cr$_3$C$_2$, CrB, CrB$_2$, MoB (tetragonal) MoB (orthorhombic), Mo$_2$B$_5$, W$_2$N, WC, WB, W$_2$B$_5$.
Others	BN, B$_4$C, RhC, RhB, PtB, IrB, CeC$_2$, TiB$_2$, BaB$_6$.

become superconducting at about 12.0°K; this value is not only the second highest transition temperature at present known but is also remarkable in view of the fact that although the metallic constituents of the first four nitrides mentioned above are themselves known to be superconducting, molybdenum metal remains normal down to 0.05°K.[35] Such behavior is not reproduced by the group 6A element immediately above molybdenum, since we found both chromium and NaCl-structure CrN to behave normally down to 1.28°K. The sudden drop in superconducting transition temperature which accompanies an increase in atomic number from 23 (V) to 24 (Cr)[36] evidently occurs, therefore, in the mononitrides as well as in the pure metals. In view of the antiferromagnetic nature of the body-centered cubic lattice proposed by Zener,[37] it may be that the disappearance of superconducting behavior with increasing atomic number is due, in the metallic case, to increased antiferromagnetic coupling. This explanation hardly seems applicable to the nitrides, however, since in both VN and CrN the metal atoms form a face-centered cubic lattice which is apparently unfavorable to antiferromagnetism.

Of the lower nitrides known to exist, we tested Mo$_2$N and W$_2$N, both of which have an NaCl type of structure with half of the interstitial positions vacant.[31] While Mo$_2$N became superconducting at about 5.0°K, W$_2$N remained normal down to 1.28°K. Although the mononitride of tungsten would be of considerable interest, this compound could not be prepared (Sec. II D).

Carbides

From resistance measurements, Meissner and Franz[2] reported that the monocarbides ZrC, NbC, TaC, MoC, and WC exhibit superconducting transitions in the ranges 4.07°–3.35°, 10.5°–10.1°, 9.5°–9.3°, 7.8°–7.6°, and 4.2°–2.5°K, respectively. Recently, however, Ziegler and Young[14] tested ZrC, TaC, and WC magnetically and found no evidence of superconducting behavior down to 1.8°K. In view of the greater reliability of the magnetic method, it seems quite likely that the early results were spurious ones caused by superconducting impurities, probably either free metal or metallic nitrides.

We tested pure samples of WC and MoC, observing that the former remained normal down to 1.28°K, in agreement with Ziegler and Young, while the latter became superconducting at 9.26°K (see Fig. 4), not too far from the transition range found by Meissner and Franz. The transition temperature of our MoC sample may be somewhat higher than that of exactly stoichio-

[31] G. Hägg, Z. Phys. Chem. B 6, 221 (1929); 7, 339 (1930); 8, 455 (1930); 12, 33 (1931).
[32] R. Kiessling, Acta Chem. Scand. 1, 893 (1947); 3, 90 and 595 (1949); 4, 146, and 209 (1950).
[33] K. Moers, Z. anorg. Chem. 198, 262 (1931).
[34] G. Hardy and J. K. Hulm, Magnetic data for pure samples (to be published in detail shortly).

[35] E. Mendoza and J. G. Thomas, Report of the International Low Temperature Conference, Oxford, England, August (1951).
[36] It has recently been found that the addition of a few percent of Cr to V greatly decreases the transition temperature, less than 20 atom percent Cr probably being adequate to completely suppress superconducting behavior. Details will be published shortly.
[37] C. Zener, Phys. Rev. 81, 440 (1951); 85, 324 (1952).

metric MoC, owing to the slight excess of carbon, which, as already mentioned, was used to prevent the formation of Mo_2C. The possibility that the superconducting behavior was due to molybdenum nitride impurities is ruled out by the complete absence of nitride lines from the x-ray pattern. Until NbC has been tested magnetically, we conclude that MoC remains the only monocarbide unambiguously known to be superconducting.

We also tested nitride-free specimens of the hexagonal lower carbides Mo_2C and W_2C, both of which became superconducting at 2.78°K and 2.74°K, respectively, in quite good agreement with resistance transitions observed in the ranges 3.2°K–2.4°K for Mo_2C by Meissner and Franz[2] and 3.5°K–2.05°K for W_2C by McLennan, Allen, and Wilhelm.[38] Both our samples gave sharp x-ray patterns which were very similar to those obtained by Westgren and Phragmen[39] and Becker[40] and which indicated that the only impurity was a small trace of WC in the tungsten compound. Since tungsten monocarbide remains normal down to 1.28°K, its presence was of no importance.

Borides

By x-ray studies of the transition metal borides, Kiessling[32, 41] found that with increasing boron content the boron atoms form successively into chains, nets, and three-dimensional frameworks, presumably through the formation of covalent bonds. In this respect the borides differ markedly from other interstitial compounds such as carbides and nitrides, among which Cr_3C_2 seems to be the only example of chain structure formation by the "metalloid" atoms. Kiessling suggested that boride formation is accompanied by a transfer of electrons from the boron chains to the metal atoms, but Pauling[42] contends that at least a fraction of an electron per atom is transferred in the opposite direction. Whichever direction the transfer, if any, takes place in, there is undoubtedly a change in metallic character with increasing boron content, a change which appears from our results to be increasingly unfavorable to superconductivity.

Commencing at the low boron content end of the range, there are several hemiborides with a tetragonal lattice of the $CuAl_2$ type containing boron atoms that are essentially isolated within groups of metal atoms. In this class we have so far tested only Mo_2B, which became superconducting at about 4.74°K (Figs. 2, 3). The x-ray pattern for this sample gave no evidence of the presence of superconducting impurities such as carbides or nitrides of molybdenum.

Among the monoborides Kiessling described three

different types of lattice which have two common features: first, the occurrence of separate boron chains; and second, the arrangement of the metal atoms in a very distorted close-packed hexagonal lattice. The orthorhombic type represented by FeB, CoB, and MnB was not examined, but we tested all known examples of the other two types, viz., orthorhombic CrB, NbB, TaB, and MoB and tetragonal MoB and WB. The only one of these compounds to exhibit superconducting behavior above 1.28°K was NbB, with a transition temperature of 8.25°K. In a previous paper[12] we reported a somewhat lower transition temperature, 6.0°K for NbB, which appears, however, to have been due to several percent of dissolved impurity, mainly molybdenum; furthermore, the superconducting transition
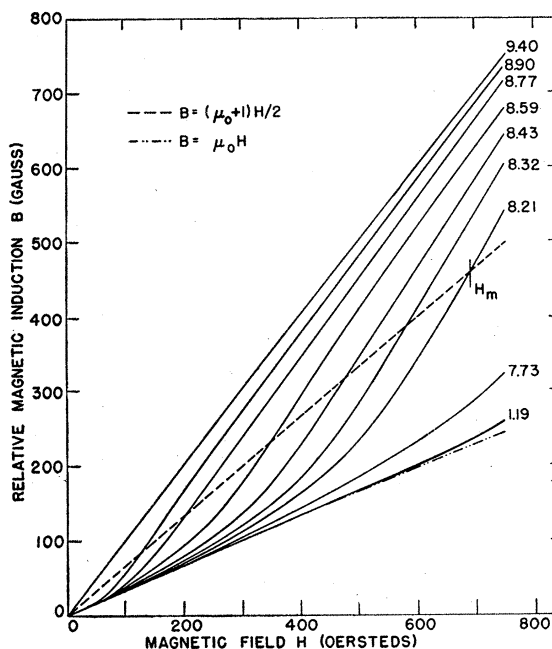

FIG. 4. Magnetic induction—magnetic field curves at various temperatures, MoC specimen.

reported at 4.4°K for MoB is now known to have been due to small amounts of Mo_2B impurity.[43]

Meissner and his co-workers[3] described resistance

[38] McLennan, Allen, and Wilhelm, Trans. Roy. Soc. (Canada) 25, Sec. 3, 1 (1931).
[39] A. Westgren and G. Phragmen, Z. anorg. Chem. 156, 31 (1926).
[40] K. Becker, Z. Physik 51, 481 (1928).
[41] R. Kiessling, J. Electrochem. Soc. 98, 166 (1951).
[42] L. Pauling, J. Electrochem. Soc. 98, 518 (1951).

[43] Our early samples were powders prepared in the induction furnace. The molybdenum boride sample was mainly tetragonal MoB but contained small amounts of Mo_2B. Since flux was excluded from about 70 percent of the volume of the sample below 4.4°K, the superconducting behavior was attributed to MoB. However, Ziegler and Young failed to confirm our result, and the question was reopened by preparing an MoB sample entirely free of Mo_2B (by melting molybdenum with 52 atomic percent of boron in the arc furnace) and also a pure Mo_2B sample. As already mentioned, the Mo_2B sample became superconducting at 4.8°K, whereas the MoB sample, containing both the tetragonal form and a metastable orthorhombic form described by R. Steinitz [J. Metals 4, 148 (1952)] remained normal down to 1.28°K. We conclude, therefore, that the behavior of the earlier molybdenum boride sample was due to Mo_2B impurities distributed so as to envelop a good deal of normal matter in a flux-excluding sheath. The danger of ignoring small amounts of impurity, even in magnetic measurements, is well brought out.

tests on the monoborides of titanium, zirconium, and hafnium which disclosed a transition in the range 3.8°–2.8°K for "ZrB." However, considerable doubt is cast on these results by the structure work of Kiessling, according to which "ZrB" does not exist and TiB tends to decompose into titanium and TiB_2 at room temperature. We found the hexagonal compound TiB_2 to behave normally down to 1.28°K, while Ziegler and Young observe normal behavior in TiB_x, ZrB_2, and ThB_2 down to 1.8°K.

Other monoborides were disclosed by the recent work of Buddery and Welch[44] on the combination of boron with the platinum group of metals, but no structural data are yet available for these compounds. We tested sintered samples of the approximate compositions PtB, RhB, and IrB down to 1.28°K, without observing superconducting behavior. Finally, no superconductors were found with a boron content appreciably greater than 50 atomic percent, presumably owing to the dominant covalent character of boron in such cases (see Table IV).

IV. CONCLUSION

The known superconductors now comprise twenty-one metallic elements, a large number of alloys and intermetallic compounds which contain at least one superconducting metal, ten intermetallic compounds of bismuth with other nonsuperconducting metals and about thirteen distinct compounds of metals with nonmetallic elements, mainly interstitial compounds of boron, carbon, and nitrogen with metals of the transition groups. The present experiments revealed new superconducting bismuthides and new interstitial superconductors, without, however, yielding new superconducting compounds of radically different types, all of which tends to support the view, based primarily on the behavior of the elements, that the superconducting phenomenon requires metallic bonding of a rather special character, so far known mainly by its localization in the periodic system.[45] Perhaps the most interesting new evidence on this character is provided by the interstitial compounds, of which the known superconductors comprise six nitrides, four carbides, and two borides, possibly indicating a decrease in superconducting tendency with decrease in the number of electrons of the "metalloid" atom. There are, unfortunately, structure differences within the interstitial series which complicate this effect.

Although the role of crystal structure remains in-

definite, we regard it as a significant fact that among the superconducting elements the transition takes place below 1°K for eight of the ten close-packed hexagonal metals and above 1°K for all of the eight cubic and tetragonal metals. This apparent tendency for transition temperatures to be lower for a hexagonal lattice than for a cubic lattice is borne out by the behavior of the nitrides, where in TiN and ZrN, for example, the metal atoms form a face-centered cubic lattice and the transition temperatures lie well above those of the close-packed hexagonal parent metals. Similarly, in the monoborides where the metal atoms form a very distorted close-packed hexagonal lattice, only NbB is known to be superconducting above 1.3°K; even in this case the transition temperature (8.25°K) is lower than that of the cubic parent metal Nb (9.3°K) or the cubic nitride NbN (14.7°K). Finally, in agreement with the above trend, mostly cubic or tetragonal symmetry has so far been found among the bismuth compounds known to be superconducting above 1°K.

Considerations of the above type could perhaps be placed on a more quantitative basis if the effects of crystal structure changes could be distinguished clearly from effects due purely to variations in the conduction electron-to-atom ratio in the normal solid. Although in a sense these two factors are inseparable, since the behavior of the conduction electrons is determined largely by the containing lattice, nevertheless, some hope is offered by the possibility of varying the number of conduction electrons per atom over a considerable range within a given type of structure. The extensively studied group B superconductors provide little opportunity in this respect, owing to the diversity of their crystal structures and their lack of interstitial compounds. A much more fruitful situation exists for the group A superconducting metals, however, since body-centered cubic, solid solution alloys are formed by the superconductors vanadium, niobium, and tantalum with up to about 80 atomic percent of their group 4A neighbors and over the complete range with their group 6A neighbors. Furthermore, the majority of the monoxides, mononitrides, and monocarbides of these metals belong to the simple NaCl lattice and presumably form wide range solid solutions among themselves. It is hoped that experiments that are now in progress on the magnetic and electrical properties of such alloys of the transition metals and their interstitial compounds will lead to a deeper understanding of the critical electronic conditions producing superconductivity.

[44] J. H. Buddery and A. J. E. Welch, Nature 167, 362 (1951).
[45] *Note added in proof:*—CoSi₂, recently found to be superconducting by one of us (B. T. Matthias, Phys. Rev. 87, 380 (1952), seems to be exceptional from this point of view.