

Studies of Compounds for Superconductivity*†

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A number of metal carbides, borides, nitrides, and a hydride, in the form of powders, have been examined for superconductivity down to 1.8°K using a magnetic method. The substances tested were TiC, VC, ZrC, TaC, WC, ZrB₂, NbB₂, TaB₂, WB, MoB, TiB₂, ThB₂, LaN, CeN, NbN, and LaH_{2.45}. All specimens were characterized by x-ray diffraction methods and, in most instances, by chemical analysis. Of these substances only NbN gave evidence for superconductivity. The results for NbN are in general agreement with the work of others. The results for TiC and VC are in agreement with those found by Meissner *et al.*, using an electrical resistance method, while those for TaB₂, NbB₂, WC, and WB are in agreement with observations made by Matthias and Hulm using a magnetic method. On the other hand, ZrC, TaC, WC, and "zirconium boride" had previously been observed to exhibit superconductivity above 1.8°K by the electrical resistance

method. The results for WC and MoB have recently been confirmed by Matthias and Hulm. The substances ThB₂, LaN, CeN, and LaH_{2.45} had not previously been examined for superconductivity.

Particle size measurements were made on the carbide and boride powders. The particles were large enough that magnetic field penetration effects should have caused no difficulty, if a penetration depth of 1×10^{-5} cm, observed for pure metal, is assumed to apply to the present compounds.

The failure to observe superconductivity in the substances ZrC, TaC, WC, and MoB in the present study is discussed in terms of a postulated physical distribution of superconducting impurities of undetermined composition which are assumed to account for the superconductivity observed in these compounds by other investigators.

INTRODUCTION

THE occurrence of superconductivity in binary compounds containing a metal and a nonmetal has been known for more than twenty years as a result of the extensive work of Meissner and his co-workers.¹⁻³ A survey of the literature has shown that in many instances the occurrence of superconductivity in compounds has been observed by studying the change of electrical resistance with temperature. In all instances in which superconductivity was observed by this means, the electrical resistance of the substance was found to decrease with temperature from room temperature to the transition temperature in the manner characteristic of metals.^{4,5} Most of the compounds found to exhibit superconductivity are binary compounds between superconducting metals and boron, carbon, or nitrogen. On the other hand, the carbides of tungsten and the carbides, a boride, and two nitrides of molybdenum also show superconducting behavior, even though the pure metals do not become superconducting at the lowest temperature tried (<1°K).

The difficulty of preparing these compounds in pure form has presented the possibility that the observed superconductivity may arise from superconducting filaments (either of the parent metal or a compound) present in the specimen rather than from the bulk specimen itself. This doubt has suggested the re-examination of these substances by means of magnetic

methods, since, as Shoenberg has pointed out,⁶ these methods should yield information concerning the behavior of the entire volume of the specimen, rather than of possible superconducting filaments.

Relatively little work has been published on the magnetic transition into superconductivity in compounds and in certain metals which are difficult to purify. Titanium specimens of various purities have been reported to have transition temperatures ranging from 1.13° to 1.77°^{2,7,8} when examined by the electrical resistance method, whereas other specimens of titanium of high purity, examined by magnetic methods, have either failed to exhibit superconductivity down to 1°K⁹ or exhibited superconductivity only at much lower temperatures (0.53°K).¹⁰ A similar situation has been reported for uranium.^{6,11}

Recently Matthias and Hulm,⁵ in an extensive survey of the occurrence of superconductivity in compounds examined by the magnetic method, have confirmed the occurrence of superconductivity in a number of compounds in which it has previously been observed using the electrical resistance test, but failed to find the effect in WC in which it had previously been observed by the resistance method.

Studies have been in progress in this laboratory for some time to re-examine by a magnetic induction method a number of compounds previously examined for superconductivity by the electrical resistance method. A number of compounds not previously tested for superconductivity are also being studied. The present paper deals with the results of studies made on fifteen metal carbides, borides, nitrides, and a hydride.

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† Based on a paper presented at the International Conference on Low Temperature Physics, Oxford, England, August 22-28 (1951).

¹ W. Meissner and H. Franz, *Z. Physik* **65**, 30 (1930).

² Meissner, Franz, and Westerhoff, *Ann. Physik* (5) **13**, 555 (1932).

³ Meissner, Franz, and Westerhoff, *Z. Physik* **75**, 521 (1932).

⁴ W. T. Ziegler, *Research Engr.* **IX**, No. 1, 15 (1947).

⁵ B. T. Matthias and J. K. Hulm, *Phys. Rev.* **87**, 799 (1952).

⁶ D. Shoenberg, *Nature* **159**, 303 (1947).

⁷ W. Meissner, *Z. Physik* **60**, 181 (1930).

⁸ W. J. de Haas and P. M. van Alphen, *Proc. Acad. Sci. Amsterdam* **34**, 70 (1931).

⁹ D. Shoenberg, *Proc. Cambridge Phil. Soc.* **36**, 84 (1940).

¹⁰ J. G. Daunt and C. V. Heer, *Phys. Rev.* **76**, 715 (1949).

¹¹ B. B. Goodman and D. Shoenberg, *Nature* **165**, 441 (1950).

TABLE I. Composition of carbides.

Metal	Calculated x in MC_x	Major constituent	X-ray diffraction analysis		
			Lattice	Reference	Minor constituents
Titanium	0.948	TiC	NaCl	12	Ti (?) ^a TaC (?)
Vanadium	0.820	VC	NaCl	12, 13	V
Zirconium	0.860	ZrC	NaCl	12	Nb and/or Ta Zr (?)
Tantalum	0.980	TaC	NaCl	12	None
Tungsten	0.989	WC	Hexagonal	14	None identified ^b

^a A question mark (?) implies a few lines corresponding to structure of this substance present.

^b W_2C absent.

The compounds studied were: TiC, VC, ZrC, WC, TaC, ZrB₂, NbB₂, TaB₂, WB, MoB, ThB₂, TiB_{*x*}, LaN, CeN, NbN, and LaH_{2.45}. The formulas given are descriptive rather than exact in that they correspond, in general, to the major constituents as identified by x-ray diffraction.

All materials were in the form of rather fine powders. They were examined by x-ray powder diffraction techniques using copper $K\alpha$ radiation. The diffraction patterns obtained were analyzed with the aid of published data. Partial chemical analyses were also available for all compounds. Detailed analyses of the materials have been included in order to characterize the materials studied as completely as possible.

Particle size measurements were made on the carbide and boride powders.

DESCRIPTION OF COMPOUNDS

A. Metal Carbides

The carbides were obtained through the courtesy of Dr. F. H. Horn, Research Laboratory, General Electric Company. They were prepared by the Carboloy Company, Inc., which provided the analyses from which the compositions in column 2 of Table I were calculated. Table I summarizes the x-ray diffraction results obtained.¹²⁻¹⁴ In each instance the major constituent was identified by comparison with the data given in the reference cited. From a consideration of the chemical analyses and x-ray diffraction results it was concluded that none of the specimens contained more than a trace of free metal. The tantalum carbide sample appeared to be essentially pure TaC. The occurrence of faint lines in the diffraction patterns of the other carbides indicated the presence of small amounts of impurities. Both vanadium carbide and zirconium carbide deviated appreciably from the simple stoichiometric formula MC .

B. Metal Borides

The metal borides, obtained from Cooper Metalurgical Associates, Cleveland, Ohio, were made by

¹² J. T. Norton and A. L. Mowry, *J. Metals* **1**, No. 2, 133 (1949).

¹³ W. Dawihl and W. Rix, *Z. anorg. u. allgem. Chem.* **244**, 191 (1940).

¹⁴ K. Becker, *Z. Physik* **51**, 481 (1928).

direct combination at high temperatures between the powdered metal and elemental boron, both of high purity. All specimens were rather finely divided dark gray powders. Table II summarizes the results of the chemical and x-ray diffraction analyses.¹⁵⁻¹⁷ The chemical analyses were supplied with the specimens.

The diffraction pattern from the thorium boride powder contained 69 lines. Of these the 19 strongest lines could be assigned to a face-centered cubic structure having an a_0 of $5.58 \pm 0.01A$. On the basis of the chemical analysis this structure has tentatively been assigned to ThB₂. A trace of thorium metal was present. Of the remaining lines a few were medium faint, the rest being faint or weaker. Many of these remaining lines could be accounted for by the presence of a small amount of ThB₆, using the lattice parameter ($a_0 = 4.32A$) given by Stackelberg and Neumann.¹⁸ However, several of the lines expected to be strongest (as judged by comparison with the published data¹⁸ for CaB₆) were absent.

The x-ray diffraction pattern of the titanium boride was compared with the very detailed study of Ehrlich¹⁶ who investigated the structure of the TiB_{*x*} system over the range $0 \leq x \leq 3$. Detailed comparison of the 23 lines obtained for this material with the work of Ehrlich indicated that the strongest lines corresponded very closely with the pattern given by Ehrlich for TiB_{*x*} where x ranged from 2 to 2.5, with a somewhat less satisfactory fit for x over the entire range 1 to 2.5. There was no evidence for free titanium.

C. Metal Nitrides and Hydride

The lanthanum and cerium nitrides were made by direct combination at 800-900°C between the rare-earth metal filings and nitrogen at one atmosphere pressure. A more detailed description of preparation and proper-

TABLE II. Composition of borides.

Metal	Calculated x in MB_x	Major constituent	X-ray diffraction analysis		
			Lattice	Reference	Minor constituents
Molybdenum	0.99	MoB	Tetragonal	15	Mo ₂ B Mo
Tungsten	1.03	WB	Tetragonal	15	None
Thorium	2.04	Not identified	Face-centered cubic		Th ThB ₆ (?) ^a
Titanium	0.99	TiB _{<i>x</i>} $x = 2-2.5$		16	None identified
Niobium	1.94	NbB ₂	Hexagonal	17	Nb
Zirconium	2.35	ZrB ₂	Hexagonal	17	None identified
Tantalum	1.75	TaB ₂	Hexagonal	17	None identified

^a A question mark implies that a few lines corresponding to the structure of this substance were present.

¹⁵ R. Kiessling, *Acta. Chem. Scand.* **4**, 209 (1950).

¹⁶ P. Ehrlich, *Z. anorg. Chem.* **259**, 1 (1949).

¹⁷ Norton, Blumenthal, and Sindeband, *J. Metals* **1**, No. 10, 749 (1949).

¹⁸ M. v. Stackelberg and F. Neumann, *Z. physik. Chem.* **19B**, 314 (1932).

ties of these materials is given in another place.¹⁹ The nitrides examined had the approximate formula $\text{LaN}_{0.97}$ (Cooper 2, Expt. 26), $\text{LaN}_{0.94}$ (Spedding 1, Expt. 29), and $\text{CeN}_{0.87}$.

The niobium nitride²⁰ was prepared by heating niobium metal powder (Fansteel, 99.9 percent Nb) for 4 to 4½ hours at 1500°C in pure dry nitrogen. X-ray examination showed it to be primarily NbN with $a_0 = 4.37 \pm 0.01$ *kx*-units.²¹ A trace of Nb and/or Ta metal appeared to be present. A large number of faint to very faint lines could not be identified. These lines did not fit the pattern for Nb₂N reported by Brauer.²²

The lanthanum hydride was prepared by direct combination between lanthanum metal filings and pure dry hydrogen gas at 210–290°C. The method used was similar to that employed for the nitride. The product examined for superconductivity had the composition $\text{LaH}_{2.45}$. Muthmann and Kraft²³ and Rossi,²⁴ using a similar method, have reported similar products having the approximate formulas LaH_3 and $\text{LaH}_{2.4}$, respectively. The hydride had an fcc lattice with $a_0 = 5.625 \pm 0.007$ *kx* units in good agreement with the value of 5.62–3 *kx* units reported by Rossi.²⁴

EXPERIMENTAL METHOD

The cryostat and measuring apparatus used was similar to that described by Horn and Ziegler.²¹ The apparatus, the temperature scale and the magnetic method employed to detect superconductivity have been described elsewhere.²⁵ Briefly, the apparatus consisted of a heavy walled copper vessel in which liquid helium was produced by the Simon expansion method. From the main helium reservoir was suspended the experimental chamber, into which helium could be condensed at will by bringing low pressure helium into contact with the main helium reservoir. The copper experimental chamber consisted of two parts, an upper section to which the thermometers were attached, and a lower section in which the specimens to be tested for superconductivity were located and on the outside of which the coils for detecting superconductivity were wound.

The temperature of the experimental chamber was measured by means of a helium gas thermometer of the type described by Mendelssohn,²⁶ except that the helium pressure was measured both by a Bourdon gauge and a capillary mercury manometer. The thermometer was

¹⁹ R. A. Young and W. T. Ziegler, *J. Am. Chem. Soc.* **74**, 5251 (1952).

²⁰ This material was prepared by Dr. F. H. Horn, General Electric Co., Schenectady, N. Y., as part of a cooperative study on Nb-Ta alloys and their nitrides.

²¹ F. H. Horn and W. T. Ziegler, *J. Am. Chem. Soc.* **69**, 2762 (1947).

²² G. Brauer, *Z. Elektrochem.* **46**, 397 (1940).

²³ W. Muthmann and K. Kraft, *Ann. Chem., Justus Liebig's* **325**, 266 (1902).

²⁴ A. Rossi, *Nature* **133**, 174 (1934).

²⁵ W. T. Ziegler and R. A. Young, *J. Am. Chem. Soc.* **March**, 1953.

²⁶ K. Mendelssohn, *Z. Physik* **73**, 482 (1931).

TABLE III. Superconductivity of metal carbides.

Carbide	Major constituent	Transition temp. ^a and range, °K		Method ^e
		This research	Lit.	
TiC _{0.95}	TiC	(1.8) ^b	1.1 (?) (1.31)	R ^d R ^e
VC _{0.82}	VC	(1.8)	(1.33)	R ^d
ZrC _{0.86}	ZrC	(1.8)	3.7	R ^e
TaC _{0.93}	TaC	(1.8)	3.3–4.1 9.3, 9.2–9.4	R ^d R ^e
WC _{0.99}	WC	(1.8)	7.6–9.5 3.4, 2.5–4.0 (1.28)	R ^d M ^f

^a Temperature corresponding to 50 percent of total resistance change in transition.

^b Temperature in parentheses means substance not superconducting down to this temperature.

^c R = electrical resistance method; M = magnetic method.

^d See reference 1.

^e See reference 3.

^f See reference 5.

calibrated by using the boiling points of hydrogen and helium and the triple point of hydrogen as fixed points. Gas imperfection was taken into account by making use of the virial coefficients given by Keesom.²⁷ The absolute accuracy of the temperature scale is believed to be about 0.05° in the range below 5°K, 0.1° in the range 5–7°K and 14–20°K, and a few tenths of a degree in the range between 7° and 14°K.

A constantan resistance thermometer, having a sensitivity of 0.01–0.02°, also was used to follow the temperature changes of the experimental chamber.

The magnetic system used for detecting superconductivity essentially measured the change in inductance produced when the specimen became superconducting. This change in inductance was measured as a galvanometer deflection produced when the primary circuit was momentarily energized. The circuits were so arranged that the galvanometer deflection could be reduced to zero at will by the suitable adjustment of a compensating inductance.

The powdered samples were generally mounted in a 7 mm o.d. Pyrex glass tube, partly open at the top end, and were in direct contact with the helium. In a few instances (TiC, VC, $\text{LaH}_{2.45}$, CeN, and LaN), the measurements were made on samples in Pyrex capsules sealed at room temperature under 20 cm Hg pressure of helium. The samples had weights varying from 0.7 to 2.5 g, and usually had a length of 20–22 mm and a diameter of 4.5–4.9 mm.

EXPERIMENTAL RESULTS

The experimental results for the various compounds tested are summarized in Tables III and IV, together with the results of other investigators.^{1,3,5,28,29} In these tables the major constituent given is that found by

²⁷ W. H. Keesom, *Helium* (Elsevier Publishing Company, New York, 1942), p. 49.

²⁸ J. K. Hulm and B. T. Matthias, *Phys. Rev.* **82**, 273 (1951).

²⁹ Aschermann, Friederich, Justi, and Kramer, *Physik. Z.* **42**, 349 (1941).

TABLE IV. Superconductivity of metal borides.

Boride	Major constituent	Transition temp. and range, °K		Method
		This research	Lit.	
MoB _{0.99}	MoB	(1.74)	(1.28)	M ^a
WB _{1.03}	WB	(1.77)	(1.28)	M ^a
ThB _{2.04}	ThB ₂	(1.77)		
TiB _{0.99}	TiB _{2-2.5}	(1.8)	(1.26)	R ^b
			(1.28)	M ^c
NbB _{1.94}	NbB ₂	(1.8)	(1.27)	M ^d
			(9.5)	R ^e
ZrB _{2.35}	ZrB ₂	(1.8)	3.1, 2.9-3.3	R ^f
TaB _{1.75}	TaB ₂	(1.8)	(1.28)	M ^{b, d}

^a See reference 5.

^b See reference 3.

^c For TiB₂, see reference 5.

^d See reference 28.

^e See reference 29.

^f For "zirconium boride," see reference 3.

x-ray diffraction analysis, while the formula given in the first column of each table is that derived from chemical analysis.

The observations of superconductivity in NbN is in general agreement with the results previously found by both the electrical resistance^{21,29,30} and magnetic induction^{21,31} methods. The transition was spread out over the range 16.8° to 14.8°K with the midpoint of the transition at 16.0°K. The sensitivity of the magnetic detection system was such that the NbN specimen gave a total galvanometer deflection of 4.2 cm in passing from the normal to the superconducting state. On the basis of this and other measurements, it was estimated that the occurrence of superconductivity could have been detected in a volume corresponding to 5-10 percent of the volume of the samples used.

The failure to observe superconductivity in TiC and VC is in agreement with the electrical resistance measurements of Meissner *et al.*^{1,3} while the absence of superconductivity in ZrC, TaC, and WC is in disagreement with the observations of these investigators. Matthias and Hulm,⁵ using a magnetic method, also found no evidence of superconductivity in WC down to 1.28°K. These investigators also reported that MoB and WB failed to become superconducting down to 1.28°K, in agreement with the results of the present work.

The failure to observe superconductivity in NbB₂ and TaB₂ is in agreement with the magnetic studies of Hulm and Matthias.²⁸ These investigators have also reported TiB₂ not to be a superconductor down to 1.28°K.⁵ We observed a similar result for a boride having the approximate composition TiB_{2-2.5}. Meissner *et al.*³ observed no transition by the resistance method down to 1.26°K in a titanium boride specimen of unstated composition. No transition was observed in ZrB₂, whereas Meissner *et al.*,³ using the resistance method, have reported a transition near 3.1°K in "zirconium boride."

³⁰ R. M. Milton, Chem. Revs. **39**, 419 (1946).

³¹ Cook, Zemansky, and Boorse, Phys. Rev. **79**, 1021 (1950).

Thorium boride, lanthanum and cerium nitrides, and lanthanum hydride were found not to be superconductors down to 1.8°K. These substances have not previously been examined for superconductivity.

The failure to observe superconductivity in the lanthanum nitrides and hydride is interesting since the transition temperatures of the two lanthanum metal specimens used to prepare the nitrides had previously been found to be 3.1° (Cooper 2) and 5.2° (Spedding 1) while that used to prepare the hydride had a transition temperature of 3.5° (Cooper 3).²⁵ The cerium metal from which the nitride was prepared was not superconducting down to 1.8°K.³²

DISCUSSION OF RESULTS

Several reasons for the failure to observe superconductivity in those compounds in which it had been observed by others suggested themselves. One was that the apparatus was not functioning properly, possibly due to thermal nonequilibrium. However, the detection of superconductivity in bulk specimens of lanthanum, lead, and tin metals, lanthanum filings and powdered NbN with the apparatus seemed to exclude this possibility.

The measurements on LaN, CeN, LaH_{2.45}, TiC, and VC were made on samples sealed in capsules under 20 cm Hg helium pressure at room temperature. The possibility that the helium gas was adsorbed at low temperatures, thus resulting in poor heat transfer, is not entirely excluded. However, experiments with lanthanum metal filings sealed under similar conditions showed no significant hysteresis in the transition at 4°K. In general, specimens were kept below 4.2°K for as long as an hour, and below the lambda-point (2.19°K) for periods ranging from 3 to 18 minutes.

The apparatus was further checked by studying a tin powder which consisted of spheres having a size range of approximately 15 to 50 microns.³³ The powder was free-flowing, and it had a yellowish appearance indicating the presence of some oxide on the surface of the tin particles. Tests of this powder gave a magnetic transition into superconductivity over the range 3.63° to 3.49°K. This is somewhat lower than the generally accepted transition temperature (3.7°K) for bulk tin. However, the calculated maximum field generated by the measuring primary was 27 oersteds, which could be expected to produce a lowering as great as 0.15°.

In order to obtain some information on the possible magnitude of field penetration effects, the particle size distribution of the carbide and boride powders was determined by measuring microscopically the linear dimensions of 100 particles which had been suitably dispersed on a glass slide. The appearance of the particles of all powders examined could best be described

³² Cerium is apparently not a superconductor down to 0.25°K. See B. B. Goodman, Nature **167**, 111 (1951).

³³ This material was obtained through the courtesy of Dr. M. C. Steele of the Naval Research Laboratory, Washington, D. C.

as roughly spherical. The particle size distribution observed is expressed in Table V in terms of the median diameter, d_g , and the geometric standard deviation, σ_g .³⁴ Calculations show that at least 50 percent of the total volume of all boride and carbide powders consisted of particles having diameters greater than one micron. It will be noted that the MoB, ZrC, and WC specimens consisted of relatively large particles. Electron-microscopic examination of the TaC powder showed that it contained a considerable fraction below one micron in size. Microscopic examination of the NbN powder showed that it was considerably coarser than the carbide and boride powders, at least 50 percent of all particles having a diameter greater than 15 microns.

The field penetration depth in powders of alloy systems such as the carbides and borides has apparently not been investigated. If one takes for the penetration depth the rough value of 1×10^{-5} cm observed in metals,³⁵ it would appear that the values of d_g for all substances studied was sufficiently large so that field penetration would not be expected to play a significant role in the present measurements.

The disagreement between the results of the present work and those of Meissner and co-workers^{1,3} regarding the occurrence of superconductivity in TaC, WC, and ZrC might be explained, as Shoenberg^{6,9} has suggested for titanium and uranium, by assuming the presence of superconducting filaments in Meissner's specimens of these carbides. Another possibility is that the transition temperatures of our carbide specimens were lowered by strain to a temperature below that reached in our experiments (1.8°).³⁶

Hudson,³⁷ using the magnetic induction method, has made an interesting study of two Sn-Ge "alloys" containing 2.3 and 9.3 atomic percent of tin, respectively, in which the tin was concentrated along the grain boundaries. These materials gave a rather broad diamagnetic transition beginning at 4°K. Hudson attributed this behavior to the presence of superconducting filaments of tin. Calculations by him indicated that approximately 50 percent of the volume of the alloy of lower tin content and the entire volume of the alloy of higher tin content participated in the magnetic transition.

In view of these observations of Hudson on the Sn-Ge alloys, it would appear that the precise physical structure of the "superconducting filaments" might be an important variable. Thus, if the filaments are thread-

TABLE V. Particle size measurements.

Substance	Borides		Substance	Carbides	
	d_g^a microns	σ_g^b		d_g microns	σ_g
NbB ₂	0.8	2.0	TaC	0.8	1.6
ThB ₂	1.1	1.4	TiC	1.3	1.9
WB	1.2	1.4	VC	1.6	2.1
TaB ₂	1.4	1.5	ZrC	2.1	2.4
TiB _x	1.5	1.6	WC	2.6	2.7
ZrB ₂	1.5	2.1			
MoB	1.7	1.9			

^a d_g = median diameter.

^b σ_g = geometric standard deviation.

like, superconductivity might be observed electrically but not magnetically. On the other hand, if the superconducting filaments possess a sponge-like structure,³⁸ with the bulk material in the holes of the sponge, as in the Ge-Sn alloy experiments of Hudson, then both an electrical and a magnetic transition might be observed. The physical structure of such filamentous inclusions might be expected to depend considerably on the method of preparation of the compound and the nature of the impurity.

The disagreement between the earlier magnetic results of Hulm and Matthias²⁸ and the present work regarding the superconductivity of MoB appears to have been due to some such sponge-like distribution of a superconducting inclusion (Mo₂B).⁵ A similar explanation has been advanced³⁹⁻⁴¹ to account for the conflicting magnetic observations of Darby *et al.*⁴² and Hudson^{39,40} regarding the superconductivity of PbS.⁴³

The possibility that superconductivity in many compounds may be due to rather specific amounts of trace impurities, distributed in a homogeneous manner through the bulk material, which makes possible a superconducting state has not been excluded.

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³⁸ K. Mendelssohn, Proc. Roy. Soc. (London) **A152**, 36 (1935).

³⁹ R. P. Hudson, Proc. NBS Semicentennial Symposium on Low Temperature Physics, Natl. Bur. Standards, Washington, D. C. March 27-29, 1951 [National Bureau of Standards Circular 519 (1952), p. 61].

⁴⁰ R. P. Hudson, Proc. Phys. Soc. (London) **A64**, 751 (1951).

⁴¹ Hatton, Rollin, and Seymour, Proc. Phys. Soc. (London) **A64**, 667 (1951).

⁴² Darby, Hatton, and Rollin, Proc. Phys. Soc. (London) **A63**, 1181 (1950).

⁴³ This explanation came to our attention after the presentation of our paper at the Oxford Conference.

³⁴ J. M. DallaValle, *Micromeritics: The Technology of Fine Particles* (Pitman Publishing Company, New York, 1948), Chapter 3.

³⁵ F. London, *Superfluids* (John Wiley and Sons, Inc., New York, 1950), Vol. I, pp. 46, 89.

³⁶ The crystallite size may be a more important factor than the particle size in determining the effects of field penetration. The lines of the x-ray diffraction pattern for TaC were all quite diffuse indicating a small crystallite size; on the other hand, those for WC and ZrC were quite sharp.

³⁷ R. P. Hudson, Phys. Rev. **79**, 883 (1950).