[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

Superconductivity and Structure of Hydrides and Nitrides of Tantalum and Columbium[1,2]

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Introduction

The work reported here is the beginning of a series of studies directed toward disclosing superconductors with high transition temperatures. The basis used for the selection of materials for study is, at present, an empirical qualitative relation between the superconducting transition temperatures and room-temperature structure parameters of the materials. Since experiment has indicated that no detectable change in lattice structure takes place when a substance passes from the normal to the superconducting state,[5] the room temperature structure parameters may be taken as an approximation to the lattice structure at the superconducting transition.

Present considerations concern only superconductors which are interstitial alloys, that is, those alloys of the transition group metals with a small non-metal atom, such as hydrogen, boron, carbon, or nitrogen, distributed among the interstices of the metal atom lattice.

Efforts to relate the transition temperatures of superconductors to crystal structure parameters of the solid are not new. Meissner and Franz[6] made such an attempt: However, it was abandoned because the metal–metal atom distance in tantalum carbide was found to be greater than in tantalum metal, yet tantalum metal has a lower transition temperature than tantalum carbide. This was considered to be contradictory to a concept of superconductivity in which electrical conductivity is related to the ease of transfer of electrons from one metal atom to the next, for by such a process that substance in which the metal–metal atom distance is smaller would be expected to show the higher superconducting transition temperature. On the other hand, Allen[7] concluded from a study of soft-metal alloys that superconductivity is a property of the solid structure as a whole. Allen found further that for those composition ranges wherein a double series of mixed crystals was formed the superconducting transition temperature of the alloy varies inversely with the dimension of the crystal lattice parameters.

Correlation of the superconducting transition temperatures, crystal structures, and lattice parameters for superconducting transition metals and their interstitial alloys,[8] suggests the following qualitative generalization: *in a series of interstitial alloys containing the same parent metal, the superconducting transition temperature varies inversely with the dimension of the lattice parameters, provided the same crystal structure is maintained.* Two possible types of series present themselves for consideration. One of these is a series in which the per cent. of a given interstitial alloying element is varied, as in the hydrides. The other possible series is one in which the nature of the interstitial alloying element is changed, such as in the series hydride, boride, carbide, nitride.

An examination of the available data shows that for the interstitial alloys of a given metal the superconducting transition temperature increases in the order: boride, carbide, nitride. For the alloys which possess the same crystal structure, the lattice parameters decrease in the same order. The question is raised whether it is the nature of the alloying non-metal itself or whether it is the effect of the non-metal on the parent metal–metal distance which is responsible for the change in the superconducting temperature. For the present the effect of the kind of non-metal atom will be neglected; only its effect on the lattice structure and parameters is considered.

In order to put the above qualitative generalization to test, it was necessary to find interstitial alloys of the same crystal structures with either expanded or contracted lattices. From the work of Hägg[9] the hydrides of tantalum were suggested, for, according to this structure, the body-centered cubic structure of tantalum metal expands uniformly with the introduction of up to about 12 atom per cent. of hydrogen. The columbium–hydrogen system, because of the similarity of the atom radii of tantalum and columbium, might be expected to behave similarly.

For contracting lattices, the nitrides of the transition group metals were suggested since, in general, the metal–nitride lattice is smaller than that for the metal–carbide lattice with which the superconducting transition temperature may be compared. If the structure of the nitride is the same as that for the carbide, according to the relation expressed above, the nitride would have a

(1) From a dissertation submitted by F. H. Horn to the Board of University Studies of The Johns Hopkins University in conformity with the requirement for the degree of Doctor of Philosophy, June, 1942. Classification of this material during the War has necessitated postponement of publication.

(2) Portions of this paper were presented at the May, 1942, meeting of the American Physical Society and at the Spring, 1946, meeting of the American Chemical Society.

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(5) W. H. Keesom and H. K. Onnes, *Leiden Comm.* 174b (1924).

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

(7) J. F. Allen, *Phil. Mag.*, **16**, 1005 (1933).

(8) See, for instance, the summary of W. Meissner, "Handbuch der Experimental Physik," Vol. XI, Part 2, Akademische Verlagsgesellschaft m. b. H., Leipzig, 1935, p. 216 ff.

(9) G. Hägg, *Z. physik. Chem.*, **B11**, 433 (1931).

higher transition temperature than the carbide. The measured value for the face-centered cube edge a_0 for columbium carbide, CbC, is 4.40 Å.,[10] while that measured for columbium nitride, CbN, is 4.41 Å.[10] However, on the basis of the N-atom radius in most interstitial alloys[11] the columbium nitride lattice might be expected to have a parameter of 4.28 Å. If the parameter for columbium nitride is actually smaller than that for columbium carbide, then the nitride would be expected to have a transition temperature higher than that for columbium carbide, which has the highest transition temperature reported to date.

Tantalum nitride is reported to have a hexagonal (ZnS) structure.[12] Since the structures of the interstitial alloys appear to depend primarily on spatial considerations, and since the atom radii for tantalum and columbium are so nearly the same, it seemed possible that a tantalum nitride might be prepared having a face-centered cubic structure like that for columbium nitride. A tantalum nitride having such a face-centered cubic structure would be expected to have an a_0 of 4.28 Å., considerably smaller than that for tantalum carbide in which the a_0 is reported as 4.45 Å.[13,14] A face-centered cubic modification of tantalum nitride would then be expected to have a transition temperature higher than that for tantalum carbide. If the structure is hexagonal (or other than that for tantalum carbide), no prediction concerning the transition temperature may be ventured according to the empirical statement. If, on the other hand, the superconducting transition temperature depends only on the substitution of an N-atom in the lattice and not on the structure, then tantalum nitride of any structure could presumably become superconducting at a higher temperature than tantalum carbide.

The experimental part of the present work was, then, directed toward testing a qualitative generalization based on a survey of the existing data, and relating the superconducting transition temperatures of interstitial alloys of the same crystal structure and of the same parent metal inversely to the dimension of the structure lattice parameters. The hydrides of tantalum and columbium over certain compositions of homogeneity were anticipated to have transition temperatures progressively lower than those for the respective metals, because the introduction of hydrogen into the metal, although it causes no change in the kind of structure, is accompanied by progressive expansion of the metal lattice. Columbium nitride was selected for study because nitridation of columbium to columbium nitride was expected to result in a lattice similar to that of columbium carbide but with a smaller lattice parameter; it was expected to have a transition temperature higher than that for columbium carbide. Tantalum nitride was selected for study because, if it could be obtained in a crystal modification similar to that for tantalum carbide, it would be expected to have a lattice parameter smaller than that for tantalum carbide and, hence, a higher transition temperature. However, if the structure could not be altered from that reported, which is dissimilar to that for tantalum carbide, some insight would be obtained on the relative importance of over-all structure as opposed to simply the effect of the introduction of nitrogen atoms into the metal.

(10) K. Becker and F. Ebert, *Z. Physik*, **31**, 268 (1925)
(11) G. Hägg, *Z. physik. Chem.*, **B12**, 33 (1931).
(12) A. E. Van Arkel, *Physica*, **4**, 286 (1924)
(13) P. M. McKenna, *Ind. Eng. Chem.*, **28**, 767 (1936)
(14) M. Schwarz and O. Summa, *Metallwirtschaft*, **12**, 298 (1933)

Experimental

Materials.—The tantalum and columbium metals were obtained from A. D. MacKay, New York, as granular powders. The tantalum and columbium were stated to be 99.9 and 99% pure, respectively. The tantalum powder was found to have the following particle size distribution by weight: 3.49% larger than 80 mesh, 7.23% between 80 and 100 mesh, 30.32% between 100 and 200 mesh, and the remainder, 58.94%, finer than 200 mesh. For the preparation of the tantalum nitrides, tantalum powder finer than 200 mesh was used. For the preparation of the tantalum hydrides, the tantalum powder was used in its original size. The columbium metal was first converted to a hydride to make a brittle material which could be ground to reduce the granules to a fine powder. Before preparing any compounds, the metals were degassed in a vacuum oven at 800° for at least two and one-half hours.

Preparation of Samples.—The hydrides of tantalum and columbium were prepared by allowing the powdered metals to cool slowly from about 800° in a calibrated volume of hydrogen gas.[9] Electrolytic hydrogen, passed over a heated copper catalyst to remove traces of oxygen and dried over phosphorus pentoxide, was measured in a gas buret and delivered into a sealed quartz tube containing the metal sample in a porcelain boat at a temperature of 800°, initially maintained at a vacuum of 10^{-5} mm. or better. The quartz tube, the volume of which had been accurately determined, was connected to a manometer in order that a correction could be applied for the amount of unreacted hydrogen after the metal had cooled to room temperature. Leakage of hydrogen from the quartz tube was found to be negligible during the time required for the formation of a hydride. The hydrogen content of the samples was computed from the weight of metal treated and the weight of hydrogen reacted as determined from the volume of gas absorbed.

Hydrides of tantalum containing 0, 3.97, 7.54, 11.93, 25.33 and 34.37 atom per cent. hydrogen, and hydrides of columbium containing 0, 5.06, 9.89, 23.78 and 32.76 atom per cent. hydrogen were prepared.

The tantalum and columbium nitrides were prepared by the direct union of the powdered 200-mesh or finer metal in an atmosphere of pure dry nitrogen at temperatures of 1180, 1200 and about 1350° for not less than eight hours.[15,16,17]

At 1180° the nitrogen was static and resulted in nitridation of tantalum to 24.3 atom per cent. and of columbium to 27.2 atom per cent. of nitrogen. After treatment at 1200° in static nitrogen the columbium contained 44.0 atom per cent. of nitrogen. In a continually renewed atmosphere of nitrogen at 1350° the nitridation of columbium proceeded to 47.3 atom per cent. and of tantalum to 50.2 atom per cent. of nitrogen. The nitrogen analyses were made by the Dumas method.

Crystal Lattice Parameters.—The structures and the crystal lattice parameters for the ma-

(15) E. Friederich and L. Sittig, *Z. anorg. allgem. Chem.*, **143**, 127 293 (1925).
(16) M. R. Andrews, THIS JOURNAL, **54**, 1845 (1932)
(17) G. R. Brauer, *Z. Elektrochem.*, **46**, 397 (1940)

TABLE I

INTERPLANAR SPACINGS AND INTENSITIES FOR HYDRIDE SYSTEMS

Tantalum						Columbium					
Atom % H_2		0		0		23.78			32.76		
d/n	I/I_0	a_0	d/n	I/I_0	a_0	d/n	I/I_0	a_0	d/n	I/I_0	a_0
						2.431	3		2.412	2	
2.328	10	3.296	2.330	7	(3.294)	2.347	8	(3.318)	2.341	3	(3.310)
						1.808	1		1.805	1+	
						1.721	1		1.708	1−	
1.653	3	3.296	1.653	2	3.298	1.663	3	3.326	1.663	2	3.322
						1.527	1+				
						1.406	2		1.394	1	
1.348	9	3.298	1.348	4	3.300	1.361	5	3.332	1.357	1−	3.322
						1.301	1+				
						1.279	1				
						1.213	1−		1.207	1−	
1.168	4	3.296	1.166	2−	3.299	1.179	2	3.333	1.175	1	3.322
						1.091	1		1.081	1−	
1.046	6	3.296	1.045	3	3.303	1.053	3	3.329	1.052	1	3.326
						1.033	1−				
0.9554	3	3.298	0.9544	1−	3.306	0.9627	1−	3.335			
.8846	9	3.298	.8839	4	3.304	.8915	2	3.332	0.8880	1−	3.323
.8271	2	3.298									
	Av.	3.297 ± 0.001 Å.			Av. 3.302 ± 0.004 Å.			Av. 3.331 ± 0.005 Å.			Av. 3.323 ± 0.003 Å.

terials prepared were determined insofar as possible from data obtained from powder X-ray diffraction photographs. Copper K-α radiation was used for all exposures. The Hull–Davey type powder cameras were calibrated against sodium chloride. The correction factor was found to be consistent except for a minor deviation for sin θ values less than about 0.33.

The X-ray diffraction data for tantalum metal are given in Table I while the parameters for tantalum metal and tantalum hydrides are given in Table II. The a_0 values are those calculated assuming that the body-centered cubic structure for tantalum metal is retained during hydrogenation and that the diffraction planes for the first eight lines are the 110, 200, 211, 220, 310, 222, 321 and 400 planes, respectively. The relatively small deviation in the calculated a_0 values from an average value in each case appears to justify the assumption.

The effect of increasing the amount of hydrogen in the tantalum is to expand the metal lattice (a_0 = 3.297 Å.) continuously to a composition corresponding to at least that for tantalum subhydride (a_0 = 3.399 Å.). It had been expected from the work of Hägg[9] that a heterogeneous region would be found from about 12 to 33 atom per cent. hydrogen, with the latter composition represented by a hexagonal close-packed structure. No such heterogeneity was encountered in any of the hydrogenated tantalum specimens studied in this work.

The X-ray diffraction data for columbium containing 23.78 and 32.76 atom per cent. of hydrogen which resulted in an inhomogeneous product are given in Table I. The parameters for the body-centered cubic hydrides of columbium are included in Table II. It may be seen that the region of homogeneity in the hydrogenated columbium extends only slightly above 10 atom per cent. of hydrogen. Samples containing 23.78 and 32.76 atom per cent. of hydrogen showed diffraction lines for at least two crystal systems, one of which is a body-centered cubic lattice with an a_0 value almost the same as that for columbium containing 9.89 atom per cent. of hydrogen. The other structure represented, although similar in the two cases, has not been determined.

TABLE II

LATTICE PARAMETERS AND SUPERCONDUCTING TRANSITIONS FOR TANTALUM AND COLUMBIUM HYDRIDES

Composition	Transition temp. Midpoint	Transition temp. interval, °K.	a_0 for b. c. cubic lattice, Å.
Ta	4.08	0.35	3.297 ± 0.001
Ta + 3.97 H	3.62	.83	3.314 ± .002
Ta + 7.54 H	3.26	1.31	3.316 ± .003
Ta + 11.93 H	2.81	1.83	3.331 ± .004
Ta + 25.33 H	Below 1.9	..	3.365 ± .004
Ta + 34.37 H	..	..	3.399 ± .005
Cb	8.98	0.90	3.302 ± .004
Cb + 5.06 H	7.83	2.27	3.311 ± .004
Cb + 9.89 H	7.38	3.25	3.327 ± .003
Cb + 23.78 H	..	..	3.331 ± .005 (b. c. c. phase)
Cb + 32.76 H	7.28	3.17	3.323 ± .003 (b. c. c. phase)

In the region in which the hydrogenation of columbium gives a homogeneous product, from 0 to about 10 atom per cent., the body-centered cubic lattice of columbium metal expands with increasing hydrogenation.

As a result of these studies, and considering the

great advances that have been made in the purification and separation of columbium and tantalum, it seems possible that results reported by Hägg[9] for a heterogeneous region in the tantalum–hydrogen system may have been caused by a considerable amount of columbium metal in the tantalum.

The X-ray diffraction data for the most nearly stoichiometric tantalum nitride, TaN, (50.2 atom per cent. nitrogen) are reported in Table III. The diffraction spectrum is very rich. Efforts to extract from it lines which will fit the requirements for a face-centered cubic system have failed. The complexity of the diffraction spectrum is consistent with the results of other investigators,[12] but there is no general agreement in d/n values or relative intensities.

TABLE III

X-RAY DIFFRACTION DATA FOR TANTALUM NITRIDE (TaN)

d/n	I/I_0[a]	d/n	I/I_0[a]	d/n	I/I_0[a]
2.870	10	1.291	1	0.9441	1
2.574	8	1.261	1−	.9259	4
2.517	2	1.178	6	.9064	4
2.418	1	1.155	2	.8871	4
1.922	7	1.140	6	.8624	5
1.905	5	1.045	5	.8565	2
1.765	6	1.039	2	.8397	1
1.490	1	1.023	4	.8273	4
1.458	4	0.9779	5	.8136	9
1.444	7	.9687	3	.8116	4
1.326	1−	.9648	2		

[a] I/I_0 obtained by comparison with calibrated density strip.

The diffraction data for the most nearly stoichiometric sample of columbium nitride (47.3 atom per cent. nitrogen) fit a face-centered cubic lattice with a cube edge of 4.375 ± 0.004 Å. The relative intensities for the first nine lines from diffracted α radiation were 5, 5, 5, 5, 2, 2, 3, 4, 4, respectively. The columbium containing 27.2 and 44.0 atom per cent. of nitrogen gave X-ray diffraction patterns indicating heterogeneity in which one of the components was identified as the columbium nitride, CbN.

Description of the Cryostat and the Method for Following the Superconducting Transition.—The general design and operational features of the cryostat used for this study are similar to those proposed by Simon.[18] According to this design, helium gas under a pressure of about 165 atmospheres is cooled to the temperature of solid hydrogen. By expansion of the helium gas against atmospheric pressure, helium is liquefied in a suitable chamber insulated thermally by a high vacuum. The experimental chamber is suspended below the main liquid helium reservoir and is brought to the boiling point of liquid helium (4.2°K.) by condensing into it helium gas under a pressure of one to two atmospheres which is refluxed by contact with the first helium reservoir. Temperatures below that of the normal boiling point of helium are obtained by reducing the vapor pressure over the liquid helium in the experimental chamber.

The samples for study prepared in the form of powders were difficult to form into wires suitable for electrical resistance measurements. It was felt that a magnetic method would be more sensitive to composition than a resistance method, since in the latter method there is a possibility of a continuous region of low resistance short circuiting a region of higher resistance. The course of the superconducting transitions was followed by means of an induction method[19,20,21] which utilizes the change in the magnetic properties of the substances in passing from the normal to the superconducting state. In order to obviate the difficulties attending the measurement of a small change in induced current, the current induced in the secondaries surrounding superconducting materials was bucked against the induced current in a matched secondary and the difference read on a ballistic galvanometer. The field generated by the primary for all measurements was 14.42 (calculated) gauss.

Figure 1 shows a cross-section drawing of the cryostat. The hydrogen cryostat is a large glass Dewar vessel (D) which is wrapped in hair matting and encased in a heavy-walled brass container. Fitting into the top portion of the Dewar vessel is a metal container for liquid nitrogen (N) which acts as the first thermal dam between room temperature and the low temperature parts of the apparatus. Through this container pass a Dewar tube (F) used for admitting the refrigerants, and a tube (HV) for removing the vapor of the boiling liquids. Through the inside of the tube (HV) passes a small tube extending to the inside bottom of the large outside Dewar vessel (D). This tube serves to remove the liquid nitrogen from the Dewar vessel (D) prior to admitting liquid hydrogen. Tubes are provided for admitting high pressure helium gas to, and subsequently expanding high pressure helium gas from, the main helium chamber (B), and for admitting low pressure helium gas to the experimental chamber (EC). These tubes spiral through the liquid nitrogen container. The vacuum compartment (H) is connected to the vacuum pumping system through the supporting tube (V). This tube serves also as the conduit for all electrical leads within the vacuum compartment. The wires enter the apparatus at (C) through a de Khotinsky wax seal.

Above the main helium chamber (B), the high and low pressure helium gas tubes spiral together to form a heat interchanger. The high pressure tube enters the main helium chamber at the top. The low pressure reflux gas tube (CT) passes in

(18) F. Simon, *Proc. Intern. Congr. Refrig., 7th Congr. The Hague*, Amsterdam, 1936.

(19) F. G. A. Tarr and W. O. Wilhelm, *Can. J. Research*, **12**, 265 (1935).

(20) K. Mendelssohn, *Proc. Roy. Soc.* (*London*), **A155**, 558 (1936).

(21) A. D. Misener, *ibid.*, **174**, 262 (1940).

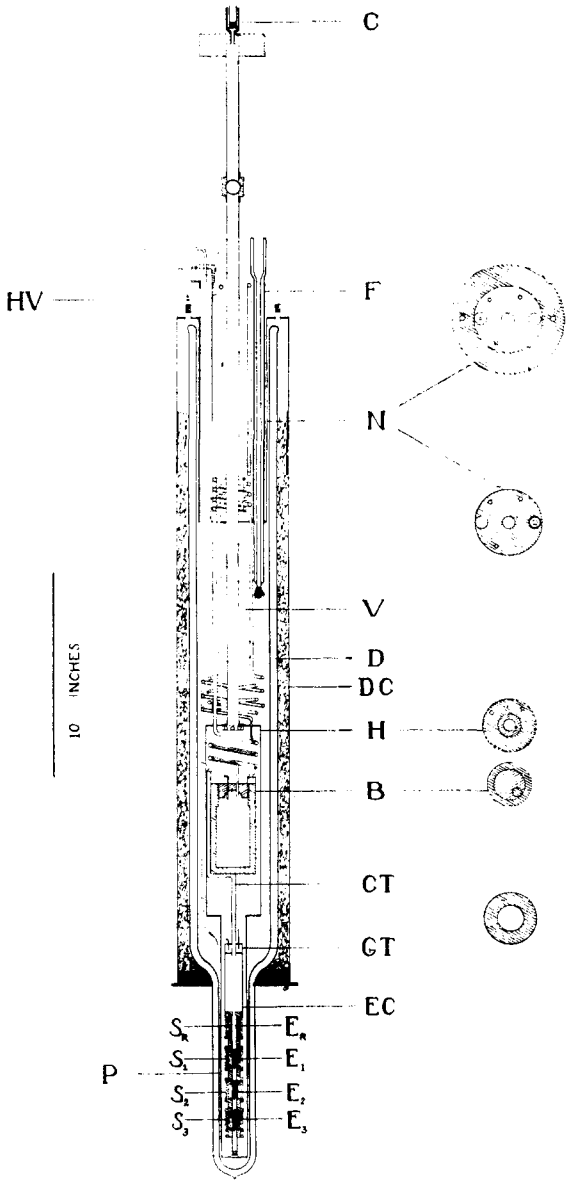

Fig. 1.

thermal contact down the side and across the bottom of the main helium chamber and, after passing through the gas thermometer reservoir (GT), enters the top of the experimental chamber (EC). The low pressure reflux tube serves as a vacuum line when it is desired to reduce the helium vapor pressure in order to reach temperatures below 4.2°K. In order to obtain temperatures below 2.2°K. (the λ-point of helium), a "creep" constriction,[22] 0.5 mm. in diameter and 1.3 cm. long, was placed in the reflux tube at a point just above the top of the experimental chamber (EC).

The four secondary coils are shown wound on the lower portion of the experimental chamber. The reference coil (E_R) and the three probe coils E_1, E_2 and E_3, with samples S_1, S_2 and S_3, respectively, at their cores, are supported on a copper tube within the experimental chamber. The primary coil (P) is wound on the outside of the lower portion of the vacuum compartment.

In the temperature range from about 14 to 20°K. the calibration of the constantan resistance thermometer, wound around the outside of EC, was carried out against a hydrogen vapor pressure thermometer filled with hydrogen gas distilled from pure liquid hydrogen. Corrections for room temperature, gravity, capillarity, and barometric pressure were applied to the readings from an open-end mercury manometer. Temperatures corresponding to the corrected hydrogen vapor pressures were calculated from the equation and constants given by Burton.[23]

In the temperature range from about 3.2 to 9°K., a helium gas thermometer was used in the manner described by Woodcock.[24]

In the temperature range from about 1.8 to 2.8°K. the calibration was against a helium vapor pressure thermometer. Temperatures were obtained from the corrected manometer readings, using the vapor pressure–temperature function given by Schmidt and Keesom.[25]

From a consideration of the errors in the gas thermometers used for calibrating the resistance thermometer, it is estimated that the recorded temperatures in the range from 1.88 to 5°K. and from 14 to 20°K. are accurate in an absolute sense to within 0.1°. In the range from about 5 to 9°K., the accuracy is of the order of 0.1°, with decreasing accuracy at higher temperatures. The reproducibility of the temperatures based on the resistance thermometer was better than 0.01°.

Measurement of Superconducting Transitions.—The curves for the course of the superconducting transitions for the tantalum hydrides measured in a magnetic field of 14.42 gauss are shown in Fig. 2, the magnetic data being reported as a percentage change in magnetic induction. Data taken from these curves are summarized in Table II, where the temperatures for the beginning and end of the superconducting transition have been chosen as those at which the induction is 98 and 2%, respectively, of that of the substance in the normal state.

In general, a slower and more uniform rate of change in temperature with time was obtainable on allowing the cryostat to warm than upon cooling. For this reason most of the points were taken during warming. In a temperature region where slow cooling could be produced by regulated reduced pressure, as for curves (2), (3) and (4), the points taken during cooling or upon warming fell within experimental error on the same curves.

(22) B. S. Blaisse, A. H. Cooke and R. A. Hull, *Physica*, **6**, 23 (1939).

(23) Burton, Grayson-Smith and Wilhelm, "Phenomena at the Temperature of Liquid Helium," Reinhold Publishing Corp., New York, N. Y., 1940, p. 51.

(24) A. H. Woodcock, *Can. J. Research*, **16A**, 133 (1938).

(25) G. Schmidt and W. Keesom, *Physica*, **4**, 963 (1937).

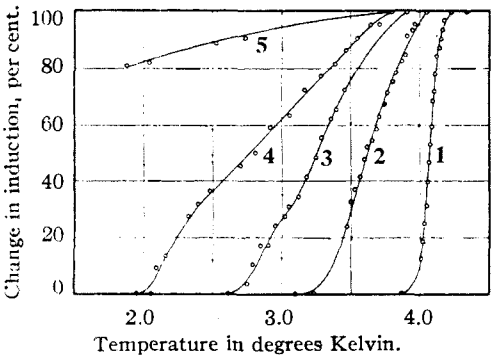

Fig. 2.—Superconducting transitions for hydrides of tantalum: curve 1, tantalum metal; 2, Ta + 3.97% H; 3, Ta + 7.54% H; 4, Ta + 11.93% H; 5, Ta + 25.33% H.

The effect of an increased amount of hydrogen in the tantalum lattice appears to be twofold. First, the temperature at which the onset of superconductivity appears is depressed. Secondly, there is an increase in the temperature range required for the material to become completely superconducting.

The superconducting transition curves for the hydrides of columbium studied during warming and measured in a field of 14.42 gauss are shown in Fig. 3. The data taken from these transition curves are summarized in Table II. As for the tantalum hydrides, an increased hydrogen content for the columbium hydrides, in general, both depresses the temperature at which superconductivity begins and increases the temperature interval required for complete superconductivity. In contrast, however, the transitions appear to crowd toward that for the columbium hydride corresponding closely to the formula Cb_2H.

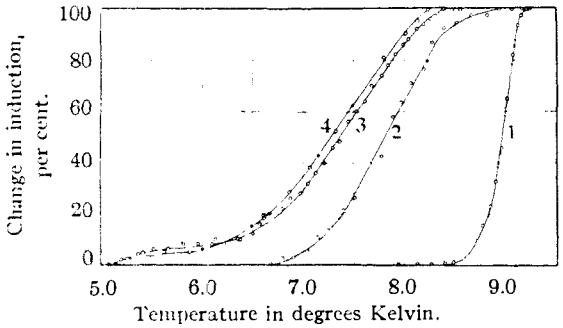

Fig. 3.—Superconducting transitions for hydrides of columbium: curve 1, columbium metal; 2, Cb + 5.06% H; 3, Cb + 9.89% H; 4, Cb + 32.76% H.

Samples of tantalum containing 24.3 and 50.2 atom per cent. of nitrogen (the latter approximating TaN) were found not to be superconducting above a temperature of 1.88°K., the lowest temperature reached in these experiments.

Superconducting transition curves for the three samples of nitrided columbium, one corresponding closely to CbN, are shown in Fig. 4. In one study, a sample of material giving curve (b) made in the form of a compressed powder changed its electrical resistance from 10.4 to 0.4 ohms in going from the normal to the superconducting state. The transition curve (a) was the same within experimental error whether measured during slow warming or cooling. Curves (b) and (c) were obtained during warming only.

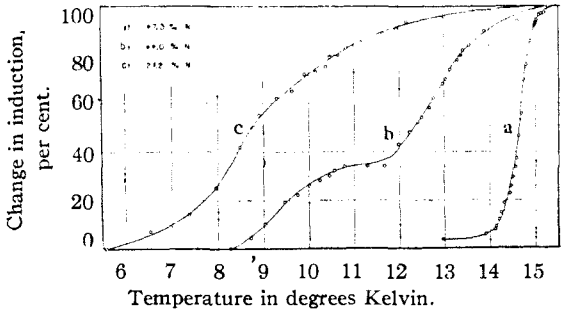

Fig. 4.—Superconducting transitions for nitrides of columbium.

The superconductivity of the CbN sample begins at a temperature of about 15.25°K.; the midpoint for the principal part of the transition falls at about 14.7°K. This is the highest transition temperature reported for a superconductor to this time,[26] being almost five degrees higher than that for CbC (10.3°K.)[7] (found by electrical resistance measurements).

Discussion of Results

Increasing hydrogenation of tantalum, to a composition corresponding to at least Ta_2H, which produces no alteration from the body-centered cubic crystal structure for tantalum metal, progressively increases the dimension of the crystal lattice. This is accompanied by two effects in the superconducting transitions: (1) a progressive depression of the temperature at which superconductivity begins, and (2) a progressive increase in the temperature range required for complete superconductivity to be realized. The first of these effects is in accord with the empirical rule set forth in the Introduction, namely, that for an interstitial alloy system wherein the crystal structure of the metal is retained, the superconducting transition temperature is related inversely to the size of the lattice parameters. The second effect is similar to that which has been described for alloy systems in general and is probably associated with the effect of the addition of "impurity" atoms to a metal.

(26) Although completed in June, 1942, and part of the work reported in May, 1942, publication during the war was withheld. Measurements on the superconductivity of columbium nitride were made in February, 1942. Because of circumstances arising from the war, the work on the superconductivity of columbium hydride and nitride by Aschermann, Friederich, Justi and Kramer (*Physik. Z.*, **42**, 349 (1941)), was not available in this country. An abstract of the work of Aschermann, *et al.*, appeared August 20, 1942 (*C. A.*, **36**, 4745 (1942)).

In the homogeneous region of solubility of hydrogen in columbium, the same two effects are noticed as in the case for the hydrides of tantalum. When the structure of the hydride becomes different from that of the metal, as in the case for the sample containing 32.76 atom per cent. of hydrogen, the temperature at which superconductivity begins is not very different from that observed for the last sample in the homogeneous structure region, 9.89 atom per cent. hydrogen (8.24 and 8.4°K., respectively), nor is the transition temperature interval greatly different (3.17 and 3.25°, respectively.) The 32.76 atom per cent. hydrogen sample consisted, in part at least, of material having a body-centered cubic structure, the lattice of which was only slightly larger than that for columbium containing 9.89 atom per cent of hydrogen. From these considerations it seems possible that the body-centered cubic material (even in the heterogenous materials) becomes superconducting and that the hydride which assumes a totally different (as yet unestablished) structure does not.

Tantalum nitride, TaN, was found to give a complex X-ray diffraction pattern. None of the diffraction lines could be selected to fit a face-centered cubic lattice. Based on the face-centered cubic tantalum carbide, TaC, which is a superconductor, no prediction could therefore be made for the superconductivity of tantalum nitride according to the empirical rule. Tantalum nitride was found not to be superconducting above 1.88°K., the lowest temperature reached. The complete change in structure here is associated either with a very marked depression of the superconducting transition temperature or with the complete destruction of superconductivity. Thus, all M–X type nitrides of superconducting interstitial alloying metals are not necessarily superconductors with higher transition temperatures than for the corresponding carbides. The lattice structure is apparently of importance in conferring superconducting properties.

Columbium nitride, CbN, was found to possess the same (face-centered cubic) structure as columbium carbide, CbC. The lattice parameter was determined to be smaller in columbium nitride (4.375 Å.) than that reported for columbium carbide, CbC (4.40 Å.). In accord with the empirical rule under test, the superconducting transition temperature for columbium nitride (beginning at 15.25°K.), was found to be considerably higher than that for columbium carbide (10.3°K.), which was prior to this time the substance with the highest superconducting transition temperature.

In the case of the hydrides of tantalum, the superconducting transition temperature is a nearly linear inverse function of the lattice parameters. In a series of contracting lattices in which the contraction is produced by the introduction of a different metalloid atom there is an apparent increase in the sensitivity of the transition temperature to the lattice parameter as successively B, C, or N is substituted. This may be seen, for instance, in the series ZrB, ZrC, ZrN in which the lattice in each case is the sodium chloride type with a_0 = 4.90 (calcd.), 4.687 and 4.63 Å. and the transition temperature ranges are 2.88–3.2, 4.32–4.1 and 9.3–9.6°K., respectively. The kind of metalloid atom in the interstices is of importance in determining the superconducting transition temperature. Its effect, the magnitude of which cannot yet be evaluated, may be neglected, as has been done in these considerations, only in trying to obtain a zero-th order approximation for the transition temperature.

In all of the present work, the emphasis has been on relations existing between structure, lattice parameters, and the superconducting transition temperatures. Although they may indeed be directly related, it is not overlooked that the structures and lattice parameters may be no more than convenient indexes of more subtle conditions, such as the lattice energy or the electron bonding, which are responsible for the property of superconductivity and for the temperatures for the onset of superconductivity. It is hoped that further work now in progress will not only disclose new superconductors but will also contribute to the theory of solids and the origins of superconductivity.

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Summary

1. A survey of the published data on the superconducting interstitial alloys has led to the formulation of the following qualitative generalization: *in a series of interstitial alloys containing the same parent metal, the superconducting transition temperature varies inversely with the dimension of the lattice parameters, provided the same crystal structure is maintained.*

2. Studies of the superconductivity of hydrides of tantalum and columbium and of columbium nitride, CbN, by a magnetic method have shown that, as predicted, the superconducting transition temperatures of these substances de-

crease continuously with increasing lattice parameter.

3. The structures of the systems hydrogen–tantalum, hydrogen–columbium, and for tantalum nitride, and columbium nitride have been investigated by means of X-ray diffraction.

4. Columbium nitride, CbN, was found to become a superconductor at 15.2°K. the highest transition temperature reported to this time for any superconductor.

5. Tantalum nitride, TaN, was found not to be a superconductor above 1.88°K., the lowest temperature reached.

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[CONTRIBUTION FROM THE CLINTON NATIONAL LABORATORY]

Ion-Exchange as a Separations Method. I. The Separation of Fission-Produced Radioisotopes, Including Individual Rare Earths, by Complexing Elution from Amberlite Resin[1]

BY EDWARD R. TOMPKINS, JOSEPH X. KHYM AND WALDO E. COHN

Introduction

It was necessary for the Plutonium Project to isolate the major fission species in the forms, purities and amounts needed for the solution of the physical, chemical and biological problems raised by the quantity production of plutonium. The stimulus to the work reported here actually came from the need to assess the radiotoxicological[1a] hazards of the fission products. The investigation of the toxicity of these elements required the biological testing of each one in the carrier-free[2] form in which it would be encountered in the plutonium process, while the large variations in biochemical behavior among the fission product elements themselves imposed exceedingly high purity specifications on each.

The major radioactive fission species (*i. e.*, those of high fission yield, of half-life greater than one week and having measurable radiations) which contain practically all of the radioactivity remaining after about thirty days of decay are listed in Table I. Together with the stable species isotopic with them, they make up 70% of the total mass of the fission products. (The residual 30% of the fission product mass is made up principally of stable Rb, Mo, Rh, Pd, La, Sm and Eu.) The separation of these fission products was required to be nearly quantitative,[3] not only for the sake of economy but in order to prevent contamination of each radioelement by the others. Finally, the multicurie activities made remote-control adaptability an essential feature of any method developed. The process described in this paper was developed specifically to separate 0.1–1 curie[4] quantities of each of the major fission species in radiochemically and chemically pure form and without resort to carrier materials. The principle which was applied to the solution of this problem has led[4a] to the discovery of a new and powerful

TABLE I[a]

RELATIVE AMOUNTS OF MAJOR RADIOACTIVE FISSION PRODUCTS COEXISTING IN URANIUM ABOUT ONE MONTH FROM THE END OF A SEVERAL MONTH EXPOSURE IN A CHAIN-REACTING PILE

Element	Total mass, mg.[b]	Radioisotopes: Mass no.	Half-life[c]	Curies
Sr	0.44	89	53 d	1.0
		90	25 y	0.035[d]
Y	0.22	91	57 d	1.25
Zr	1.2	95	65 d	1.35
Cb	0.35	95	35 d	1.7
43	.3	99	1.5×10^6 y	0.7×10^{-6}
Ru	.65	103	42 d	0.9
		106	1 y	.065[d]
Te	.16	127	90 d	.0075
		129	32 d	.03
I	.075	131	8 d	.065
Cs	1.1	137	33 y	.032
Ba	0.47	140	12.5 d	.35[d]
Ce	1.12	141	28 d	1.0
		144	275 d	0.85
Pr	0.4	143	13.8 d	0.4
Nd	1.34	147	11 d	0.12
61	0.17	147	3.7 y	0.14

[a] Calculated by W. E. Cohn from data in THIS JOURNAL, **68**, 2411 (1946). [b] Includes all isotopes arising from fission whether stable or radioactive. [c] d = days; y = years. [d] Radiations of short-lived daughter not included.

(1) This work was done at Clinton Laboratories, a part of the Plutonium Project, during the period October, 1943, to June, 1945, and is based on work performed under Contract No. W-7405-eng-39 for the Manhattan Project. The information covered herein will appear in Division IV of the Manhattan Project Technical Series as part of the contribution of Clinton Laboratories.

(1a) The study of toxicology due to the radiation, not the chemical action, of chemical entities is termed "radiotoxicology."

(2) As used in this and subsequent papers, this term means that no stable isotope is knowingly added. Stable isotopes produced in fission are, of course, always present and the presence of isotopic impurities in the original uranium and in reagents is always assumed to be likely.

(3) The specifications actually set were: 0.1–1.0 curie amounts of each major fission product per cycle, free of added carrier; radiochemical purity of 95–98% (depending on the element in question); total solids below 1 mg. per 100 ml.; no visible precipitates at *p*H 4 and no sulfide-insoluble metals

(4) One curie of a given species is defined as that amount of the species which exhibits 3.7×10^{10} disintegrations per second.

(4a) The history of the development of ion-exchange separations within the Manhattan Project is given by Johnston, Quill and Daniels, *Chem. Eng. News*, **25**, 2494 (1947).