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The Superconductivity of Columbium

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Isothermal critical magnetic field curves and zero field transitions for several annealed specimens of columbium have been measured by an a.c. mutual inductance method, at temperatures from 5.1°K to the zero field transition temperature. The $H-T$ curve was found to fit the usual parabolic relationship $H=H_0(1-T^2/T_0^2)$ with $H_0=8250$ oersteds and $T_0=8.65$°K. The initial slope of the curve was 1910 oersteds/deg. The electronic specific heat in the normal state calculated from the thermodynamic equations is $0.0375T$ and the approximate Debye characteristic temperature in the superconducting state, 67°K. Results on a different grade of columbium with a tantalum impurity of 0.4 percent, according to neutron scattering measurements, were in agreement with the data obtained from columbium of 0.2 percent maximum tantalum impurity.

I. INTRODUCTION

The superconductivity of columbium was discovered by Meissner and Franz[1] who observed that the transition from the superconducting state to the normal state occurred between 8.18° and 8.74°K on a specimen of columbium containing 1.5 percent tin. On a specimen with reported impurities of 0.08 percent O and 0.02 percent Ta Meissner, Franz, and Westerhoff[2] observed the transition to occur between 9.20° and 9.35°K. Further observations of the transition by Bruksch, Ziegler, and Hickman[3] disclosed wide variations between three specimens which gave 5.09°, 8.64°, and 9.58° respectively. These investigators searched for impurities by the x-ray method which disclosed only a removable surface contamination of SiC. Transitions in magnetic fields were measured only in the liquid helium region, 1.4° to 4.2°K, by Daunt and Mendelssohn,[4] on a specimen of "about 99.8 percent purity."

II. PURITY OF COLUMBIUM

The lack of agreement among the transition temperatures suggests a greater variation of purity among the samples of columbium than is apparent from the numerical values of purity reported by the various investigators. It is difficult not only to obtain pure columbium, but also to measure accurately the purity of any given sample.

In the natural ores columbium is found in close association with the element tantalum. The chemical properties of the two are very similar and strict quantitative separation as well as the analysis of minute amounts of tantalum in columbium are problems to which no satisfactory solution has been found. Chemically the best method involves the difference of behavior of oxalotantalic and oxalocolumbic acids in dilute solutions of tannin. Other impurities have first to be removed by long and involved procedures.[5]

The spectra of the two elements are also very difficult to resolve from each other. The columbium lines interfere with tantalum lines to such a degree that the deliberate addition of tantalum to supposedly pure columbium cannot be detected until approximately 0.2 percent has been added.

Analysis by mass spectroscopy is a possibility but would have to be done without the convenience of using a gaseous compound to supply ions. X-ray examination of the crystal lattice is not suitable for analytical work, since the lattice spacings of columbium and tantalum are respectively 3.294 and 3.296A.[6]

It therefore appears that the spectrographic method is about as sensitive as any other for determining small tantalum impurities, and it has the advantage of providing a rapid means of surveying for other impurities.

The Fansteel Corporation, which appears to be the only refiner of columbium in this country, was reported to have improved the purity of its columbium production during the war. Therefore it was considered desirable to investigate the superconducting properties of this material, inasmuch as columbium has the highest superconducting temperature of any element and its $H-T$ curve had not been studied above 4.2°K.

The specimens used in this research were supplied by the Fansteel Corporation as Lot Cb-22 in 1947, with the maximum impurities quoted as 0.20 percent tantalum, 0.03 percent silicon, 0.01 percent iron, and 0.002 percent titanium. A spectrographic survey was conducted on this material using a comparison sample from the National Bureau of Standards (B. S. S. Steel No. 123) which contained known amounts of the following elements: Ag, Al, As, B, Be, Ca, Cb, Co, Cu, Mn, Mo, Ni, P, Si, Sn, Ta, Ti, V, W, and Zr. The only im-

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‡ Assisted by the ONR.

[1] W. Meissner and H. Franz, Zeits. f. Physik **63**, 558 (1930).

[2] Meissner, Franz, and Westerhoff, Ann. d. Physik **17**, 593 (1933).

[3] Bruksch, Ziegler, and Hickman, Phys. Rev. **42**, 554 (1942).

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

[5] W. R. Schoeller, *The Analytical Chemistry of Tantalum and Niobium* (Chapman and Hall, Ltd., London, 1937). Also W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis* (John Wiley and Sons, Inc., New York, 1929), Chapter 38.

[6] Fansteel Corporation, Technical Bulletin on Columbium (1946).

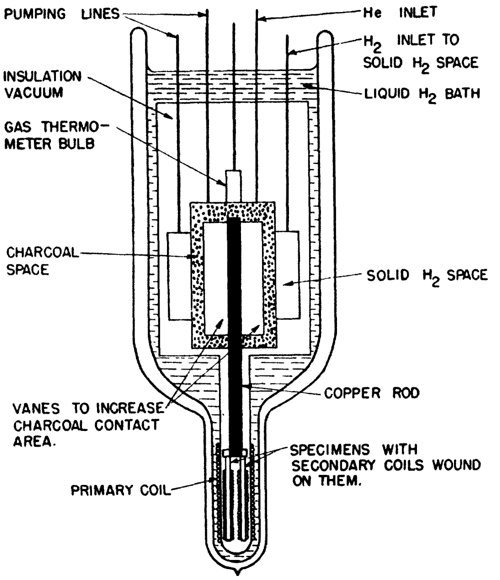

FIG. 1. Schematic diagram of the desorption cryostat.

purities indicated from the survey were iron and molybdenum, both exceedingly faint, and reported as not present in greater amounts than 0.1 percent.

A specimen of columbium produced by Fansteel prior to 1947 had been tested by means of the low velocity neutron spectrometer by Wu, Rainwater, and Havens.[7] One dip had been observed in the curve of transmission *versus* time of flight which coincided in energy value with the location of a large dip in tantalum. From the area of the weak dip in columbium it was estimated that the tantalum impurity might be 0.4 percent. From spectrographic evidence, a maximum of 1 percent of tantalum had been reported. A sample of this material was used for experimental comparison with the newer samples of columbium. After experimental data had shown the two materials to have the same superconducting properties in the annealed condition, a careful spectrographic comparison yielded the conclusion that the tantalum content was the same in both cases and of the order of 0.2 percent.

III. CRYOSTAT

To produce temperatures between 5 and 9°K required for this investigation, a helium desorption cryostat[8] was constructed, a schematic view of which is given in Fig. 1. The operation was briefly as follows: While liquid hydrogen was being transferred into the apparatus, the insulation vacuum space was filled with a few mm of helium gas to provide thermal contact between the hydrogen bath and the inner components of the apparatus. The latter consisted of concentric copper cylinders to which were attached a gas thermometer bulb and the specimens to be measured. The inner of the two concentric cylinders contained 200 cm^3 of activated charcoal (Columbia 6-G, 8–14 mesh) supplied through the courtesy of Dr. L. I. Dana of the Linde Air Products Company. During the period of cooling through hydrogen temperatures, purified helium gas was adsorbed on the charcoal at pressures up to 50 lb./sq. in.

When thermal equilibrium at 20.4°K had been reached, the gas thermometer system was filled with helium to 1 atmos. pressure. Some of the liquid hydrogen from the outer bath was then admitted to the annular space surrounding the charcoal cylinder, by means of a small valve manipulated by a retractable rod. A high vacuum was then established in the insulation-vacuum container, and the internal apparatus, thus thermally isolated from the 20.4° bath, was cooled to 10° by pumping on the liquid hydrogen in the annular space. Adsorption of helium was continued during this operation.

When equilibrium at 10° had been reached, helium was desorbed from the charcoal by a fast mechanical pump. The lowest temperature attained varied from 4.9° upwards, depending upon the rate of pumping and the amount of solid hydrogen remaining to be cooled down with the apparatus. At maximum pumping speed the minimum temperature was reached in about 10 minutes. The temperature would remain constant for a few minutes and then would rise under continued pumping at an average rate of 0.007 deg./min. Temperatures could be held constant within 0.01° for long periods provided less gas was desorbed initially, thus conserving more of the available refrigeration for control purposes. One desorption cycle was sufficient for at least three hours of experimentation, provided the outer liquid hydrogen bath was maintained at the approximate level indicated in Fig. 1.

IV. THERMOMETRY

Since vapor pressure methods of thermometry are not available between 5° and 9°, a helium gas thermometer was used to measure temperatures directly. The gas thermometer consisted of a bulb of volume 3.862 cm^3, made of an alloy of 96 percent silver and 4 percent copper, the silver being chosen because of its minimal tendency to adsorb helium on its surface, and copper added to improve machinability. The bulb was attached to the top of the desorption chamber and connected to a constant volume mercury manometer through a capillary tube of 0.4-mm bore.

Neglecting, as a first approximation, the volume and temperature gradients in the capillary, the gas thermometer may be regarded as consisting of two volumes; V_b, that of the bulb, and V_r, that at room temperature. Since gas pressures in the thermometer system were at most 1 atmos., the gas law could be taken, with sufficient accuracy, to include only the second virial

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[7] Wu, Rainwater, and Havens, Phys. Rev. 71, 174 (1947).

[8] F. Simon, Physik Zeits. 27, 790 (1926).

coefficient. Thus, at the filling temperature T_f,

$$\left.\begin{aligned} p_fV_b&=n_b(RT_f+B_fp_f),\\ \text{and}\qquad p_fV_r&=n_r(RT_r+B_rp_f),\end{aligned}\right\} \tag{1}$$

where the subscripts b, f, and r respectively designate values appropriate to the bulb, to the filling temperature, and to room temperature. R is the gas constant, n is the number of moles of gas in a given volume V, and B is the value of the second virial coefficient appropriate to the given temperature. When the bulb is at temperature T,

$$\left.\begin{aligned} pV_b&=n_b'(RT+B_Tp),\\ pV_r&=n_r'(RT_r+B_rp).\end{aligned}\right\} \tag{2}$$

Here the respective numbers of moles have changed but the total number of moles is the same as before, except for the very small effect of adsorption which is neglected. Therefore, since $n_b+n_r=n_b'+n_r'$,

$$\frac{p_fV_b}{T_f+(B_fp_f/R)}+\frac{p_fV_r}{T_r+(B_rp_f/R)} =\frac{pV_b}{T+(B_Tp/R)}+\frac{pV_r}{T_r+(B_rp/R)}. \tag{3}$$

Solving (3) for T and dividing all terms by V_b we obtain

$$T=\left[\frac{1}{\dfrac{p_f}{T_f+(B_fp_f/R)}+\dfrac{p_fV_r/V_b}{T_r+(B_rp_f/R)}-\dfrac{pV_r/V_b}{T_r+(B_rp/R)}}-\frac{B_T}{R}\right]p. \tag{4}$$

The dependence of thermometer sensitivity, dT/dp, on the choice of T_f and of the ratio S, defined as V_r/V_b, is seen by letting $B=0$ in Eq. (4) and differentiating T with respect to P. Thus

$$\frac{dT}{dp}=\frac{(p_f/T_f)+S(p_f/T_r)}{\{(p_f/T_f)-(S/T_r)(p_f-p)\}^2}. \tag{5}$$

From Eq. (5) it is seen that, when $S=0$, dT/dp is given by T_f/p_f. In order to make dp/dT as large as possible (dT/dp as small as possible) the filling pressure p_f was chosen as 1 atmos. and the filling temperature as 20.4°, the temperature of the liquid hydrogen bath. The room temperature volume V_r was chosen to be moderately large (28.771 cm^2; $S=6.41$) to provide a small increase in sensitivity.[9] Under the given conditions dT/dp at 7°K ($p=0.42$ atmos.) was 0.024 deg./mm Hg. The manometer was read to the nearest 0.5 mm, providing a thermometer sensitivity of 0.01°.

The filling conditions were such that the correction for gas imperfection amounted to 0.1 to 0.2°, since the filling pressure corresponded to an ice point pressure of about 13 atmos. This correction was applied by finding the difference $T-T^*$ between the true temperature T and the quantity T^* measured assuming $B=0$.

If Eq. (3) is divided by V_b, and B is set equal to zero, T^* is given by

$$T^*=\frac{p}{p_f/T_f+p_fS/T_r-pS/T_r}, \tag{6}$$

whereas $T-T^*$ is given by

$$T-T^*=\left[\frac{p_f\left(T_f+\dfrac{B_fp_f}{R}\right)\left(T_r+\dfrac{B_rp_f}{R}\right)\left(T_r+\dfrac{B_rp}{R}\right)}{p_f\left(T_r+\dfrac{B_rp_f}{R}\right)\left(T_r+\dfrac{B_rp}{R}\right)+p_fS\left(T_f+\dfrac{B_fp_f}{R}\right)\left(T_r+\dfrac{B_rp}{R}\right)-pS\left(T_f+\dfrac{B_fp_f}{R}\right)\left(T_r+\dfrac{B_rp_f}{R}\right)} -\frac{pT_fT_r}{p_fT_r-ST_f(p-p_f)}-\frac{B_Tp}{R}\right]. \tag{7}$$

The virial coefficients were obtained from the work of Keesom and Walstra,[10] the numerical magnitudes referring to the amount of gas occupying unit volume at 0°C, the pressure being expressed in atmos. The appropriate value of R is then 0.00366 atmos./deg. Since $B_r\sim 5\times 10^{-4}$, the terms B_rp/R and B_rp_f/R can be neglected with respect to T_r without introducing errors greater than 0.05 percent. The term B_fp_f/R is more important when compared with T_f, where it introduces an error of 0.25 percent if neglected. Since the precision of

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[9] A. H. Woodcock, Can. J. Research **A16**, 133 (1938).

[10] W. H. Keesom and W. K. Walstra, Physica **13**, 225 (1947).

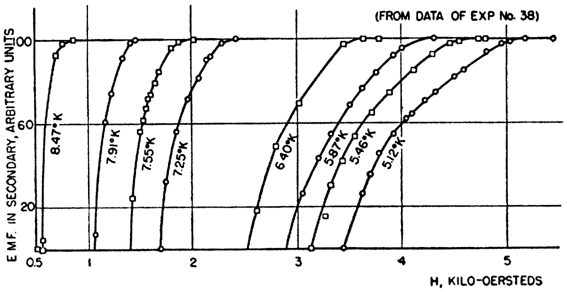

FIG. 2. Transitions of columbium cylinder in transverse fields.

the over-all experiment did not appear to warrant temperature measurements more accurate than 0.02°, and since the indicated approximations would introduce an error of no more than 0.02° at 7°K, all three aforementioned terms can be dropped in the calculations, whereupon Eq. (7) reduces to

$$T-T^{*}=-B_{T}p/R. \qquad (8)$$

The procedure involved in determining temperatures was to use Eq. (6) to determine T^{*} and then to use Eq. (8) to correct T^{*} to the true temperature T. Small correction terms were calculated to take account of the volumes of gas in the various temperature regions of the capillary tube.

The performance of the thermometer was verified at the transition temperature of lead which agreed, within the indicated accuracy, with earlier values for the lead transition in zero field.[11] The triple point of hydrogen was checked on each run. At this temperature the error introduced by neglecting $B_{f}p_{f}/R$ with respect to T_{f} was 0.03°K. The determinations averaged 13.98°K when this error was compensated for, while 13.96°K is the value for the triple point of normal hydrogen quoted by Woolley, Scott, and Brickwedde.[12]

V. METHOD

The experimental specimens were attached to the solid hydrogen and charcoal compartments of the cryostat by means of a $\frac{1}{4}$-in. copper rod which was fastened inside the charcoal space to six large copper vanes, as indicated in Fig. 1. The rod terminated at its lower end in a plate to which four specimens, each with its own secondary coil, could be attached by means of copper set screws.

In the experiments here described the transitions were measured by observation of the magnetic permeability of cylindrical samples of columbium in small alternating magnetic fields. This method, described by Webber, Reynolds, and McGuire,[13] has the advantage of requiring no electrical connections to columbium, which is difficult to solder, electroplate, or weld. The dimensions of the cylinders were 2 mm in diameter by 5 cm long. Each was used as the core of the secondary coil of a mutual inductance, the primary of which was actuated by an audio oscillator at 1000 cycles/sec. Variations of frequency between 500 and 2000 cycles/sec., as well as of amplitude over the full range available, were found to have no effect on the observed transitions. The maximum a.c. field in the secondary coil was about 5 oersteds with the oscillator set at full gain.

The e.m.f. induced in the secondary coil was dependent upon the permeability of the superconducting cylinder upon which it was wound. When the core was superconducting this secondary e.m.f. had a small residual value that was due to the flux threaded by the actual windings of the secondary. When a transition to the normal state occurred, the signal increased to a steady maximum value. The opposite change occurred in a transition from the normal to the superconducting state. The e.m.f. induced in the secondary coil was successively amplified, filtered to remove 60 cycle background, and rectified for observation on a recording potentiometer.

The bottom of the cryostat was designed to permit insertion into the pole gap of an electromagnet by means of which magnetic fields were applied transversely to the superconducting specimens. The measurement of the field at the center of the $1\frac{5}{16}$ in. gap was effected with the aid of single layer search coils of 1 cm diameter, attached to a sensitive fluxmeter calibrated by a standard mutual inductance. The absolute accuracy of determining magnetic fields was two percent or better. Hysteresis in the magnet was avoided as a systematic error by measuring magnetic transitions in the direction of increasing magnetic fields only, from the superconducting to the normal state rather than *vice versa*. Between transitions the magnet was cyclically demagnetized. For measurements of transitions in small, longitudinal magnetic fields, a solenoid was used.

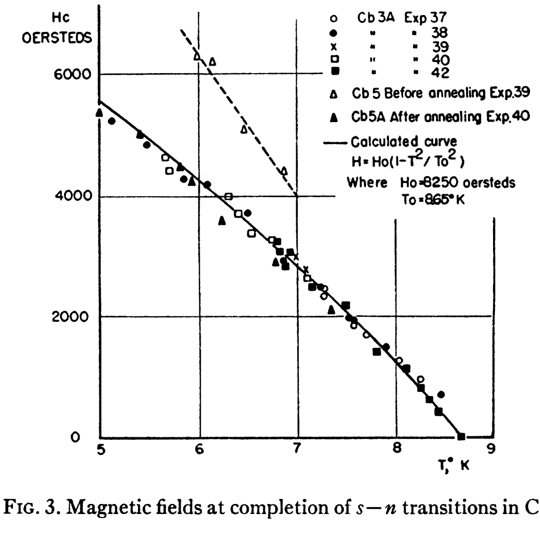

FIG. 3. Magnetic fields at completion of $s-n$ transitions in Cb.

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[11] Boorse, Cook, and Zemansky, Phys. Rev. **78**, 635 (1950).

[12] Wooley, Scott, and Brickwedde, J. Research Nat. Bur. of Stand. **41**, 379 (1948).

[13] Webber, Reynolds, and McGuire, Phys. Rev. **76**, 293 (1949).

VI. RESULTS

The measurements on columbium were made on a series of vacuum annealed samples. The detailed data given in this paper refer to the sample denoted as 3A which was given an additional heat treatment of five hours at 1000°C in a vacuum of 10^{-6} mm. The latter process was carried out at the Research Laboratory of the General Electric Company through the courtesy of Dr. F. Hubbard Horn. Two other samples annealed by Fansteel, as well as a cylindrical capsule of columbium powder were also tested and found to agree with sample 3A.

A few typical isothermal transitions in transverse magnetic fields are shown in Fig. 2. In each of the transitions the temperature was maintained constant to within 0.05°K or less. The transitions were measured in the direction of increasing magnetic fields. A number of check transitions taken in the reverse direction showed that the behavior of the sample was reversible. The critical field values are the values of H at which the sample *completes* the transition from the superconducting to the normal state. This identification is supported by the results of Webber, Reynolds, and McGuire[13] on monocrystalline tin where the $H-T$ curve thus obtained was in agreement with the generally accepted curve of de Haas and Engelkes.[14] Using a polycrystalline sample of very pure lead we have similarly verified points on the $H-T$ curve of Daunt[15] for lead.

The results of five experiments taken over a period of several months are plotted in Fig. 3. It should be emphasized that every point of Fig. 3 is the result of a complete transition curve comprising from 5 to 15 individual points. In addition to the data shown, points on the $H-T$ curve near T_0 were checked by measurements in a longitudinal field. Since the available longitudinal fields did not exceed 500 oersteds, data of this kind could be obtained only in the immediate neighborhood of T_0.

TABLE I. Successive observations of zero field transitions in columbium 3A.

Expt. no.	$T_{\frac{1}{2}n}$, °K	T_n, °K	Expt. no.	$T_{\frac{1}{2}n}$, °K	T_n, °K
37	8.98	9.08	42	8.57[a]	8.64[a]
37	8.98[a]	9.08[a]	42	8.57	8.65
42	8.56	8.64	42	8.58	8.67
42	8.56	8.66	43	8.54[a]	8.65[a]
42	8.58	8.66	43	8.53	8.66
42	8.57	8.67	43	8.54[a]	8.65[a]
42	8.59	8.66	43	8.53	8.65

		$T_{\frac{1}{2}n}$	T_n
Average values in experiments	42, 43:	8.56°K	8.65°K
Mean deviations	42, 43:	0.01°	0.01°

[a] Indicates observation on $n-s$ transition. The other points were taken on $s-n$ transitions.

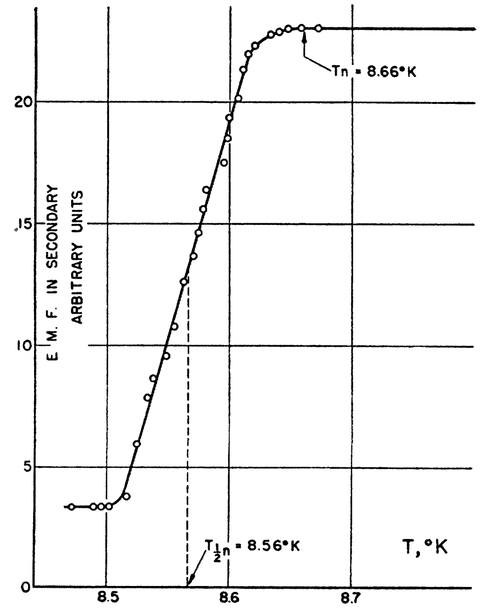

FIG. 4. Zero field transition of columbium.

The zero field transitions of this specimen had a characteristic temperature width of 0.15°K, as is shown by a typical transition plotted in Fig. 4. The traditional way of quoting the temperature value of such a transition is to give the value of the temperature $T_{\frac{1}{2}n}$ at which the transition (in resistance or permeability) has reached the half-way point between superconducting and normal values. The intersection of the $H-T$ curve with the T axis, however, can be expected to correspond not to $T_{\frac{1}{2}n}$ but to the temperature T_n at which the zero field transition to the normal state is finally completed. In cases where the transition in zero field occurs over a very narrow range of temperatures, this difference is negligible, but in the present measurements this was not the case. Therefore, in tabulating transition temperatures in Table I both $T_{\frac{1}{2}n}$ and T_n are given.

It will be noted that two values of the zero field transition were observed at $T_n=9.08°$ on the first experimental run after reannealing, whereas transitions were thereafter repeatedly observed in the neighborhood of $T_n=8.65°$. The $H-T$ curve was not displaced by this change except in the immediate vicinity of the zero field transition temperature. The value $T_n=8.65°$ was not only obtained as the result of 12 successive observations but also correlated exactly with T_0 as determined independently from the magnetic transition data assuming the parabolic law $H=H_0(1-T^2/T_0^2)$. The results with $T_n=9.08°$ are included as an indication of the experimental fact that columbium can undergo changes perhaps in the course of temperature cycling, which alter its zero field transition by a fraction of a degree without affecting the critical field properties beyond the immediate temperature neighborhood.

In the comparison experiments on the specimen of

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[14] W. J. De Haas and A. D. Engelkes, Physica 4, 325 (1937).
[15] J. G. Daunt, Phil. Mag. 28, 24 (1939).

TABLE II. Critical magnetic fields necessary to complete $s-n$ transitions in columbium containing 0.4 percent tantalum according to reference 7.

Sample No. 5 Before annealing			Sample No. 5A After annealing		
Expt. no.	T°K	H_c, kilo-oersteds	Expt. no.	T°K	H_c, kilo-oersteds
			40	5.0	5.4(2)
39	6.48	5.10	40	5.4	4.84
39	6.88	4.40	40	5.80	4.50
39	6.00	6.28	40	5.94	4.24
39	6.15	6.20	40	6.23	3.60
			40	6.80	2.88
			40	7.35	2.09

columbium 5 tested in the cyclotron experiments,[7] the first observations were made on the sample as machined into cylindrical form, and the second after annealing for three hours at 1000°C in a fused silica tube evacuated to 10^{-5} mm. The first set of $H-T$ data were higher than corresponding results in the purer specimen 3A, but after the annealing process, the results on 5A came into agreement with those of 3A. The data are given in Table II, and the complete $H-T$ curve in Fig. 3 includes these points.

VII. DISCUSSION

The $H-T$ curves of most superconductors have been observed to agree approximately with an equation of the form

$$H=H_0(1-T^2/T_0^2). \tag{9}$$

To test the validity of this equation in connection with the present results, a graph of H *versus* T^2 is shown in Fig. 5. A least squares analysis of the magnetic points alone yields the values $H_0=8250$ oersteds and $T_0=8.65$°K. It is seen therefore that this value of T_0 is in agreement with the average experimental value of T_n given in Table I for experiments 42 and 43. Values of H_0 ranging from 7280 oersteds to 8050 oersteds and of T_0 from 9.0°K to 8.71°K have been given in preliminary reports of this work.[16, 17] The values $H_0=8250$ oersteds and $T_0=8.65$°K are the result of a careful re-evaluation of all the experimental data and are believed to represent the best values obtainable from these data. The present experimental values of the critical field extrapolated to the temperature range 1 to 4°K are about three times greater than those obtained by Daunt and Mendelssohn.[4] The reason for this is by no means clear. It is to be noted that the Daunt and Mendelssohn results were obtained on a single sample of which no detailed analysis was given and the authors indicated that their experiment was of a preliminary nature.

The value of dH/dT at T_0 is 1910 oersteds/deg., which is larger than the corresponding value for any other superconductor except vanadium[13] which has a value of about 4000 oersteds/deg.** As a necessary consequence of the large values of H_0 and dH/dT at T_0, the derivable thermodynamic quantities are much larger in magnitude for columbium than for other superconducting elements. The entropy change of the transition at any given temperature T is given by

$$S(n)-S(s)=-(VH/4\pi J)dH/dT, \tag{10}$$

where V = atomic volume in cm³/mole, J = mechanical equivalent of heat, the magnetic fields are expressed in oersteds, and the entropy change is calculated in units of cal./mole deg.

In the case of columbium, the atomic weight is 92.91, which divided by the density determined for our specimens, 8.55, gives 10.87 cm³/mole. Substituting the experimental values of H_0 and T_0 in Eq. (9) we find that

$$H=8250-110T^2,$$
$$dH/dT=220T.$$

Substitution of these values into Eq. (10) leads to the result

$$S(n)-S(s)=0.0375T-0.00100T^3.$$

The change of specific heats $C_p(n)-C_p(s)$ between the two states is derived from Eq. (10) as

$$C_p(n)-C_p(s) = (VT/4\pi J)\{(dH/dT)^2+H(d^2H/dT^2)\}. \tag{11}$$

When the experimental values are substituted into Eq. (11), the difference between the two specific heats becomes

$$C_p(n)-C_p(s)=0.0375T+0.00150T^3. \tag{12}$$

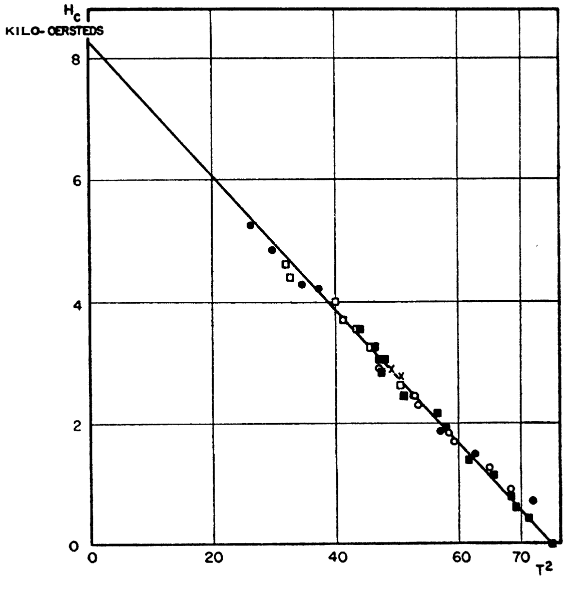

FIG. 5. Verification of the parabolic relation.

** *Note added in proof:* Since this paper was submitted, the $H-T$ curve of vanadium was determined by A. Wexler and W. S. Corak, Phys. Rev. **79**, 737 (1950), who give the value dH/dT = 400 oersteds/deg.

[16] Cook, Zemansky, and Boorse, Phys. Rev. **79**, 212 (1950).

[17] Cook Zemansky, and Boorse, Phys. Rev. **78**, 820 (1950).

The specific heat $C_p(n)$ of a metal in the normal state and at low temperatures can be expressed in the form

$$C_p(n)=\gamma T+464.4T^3/\Theta_n^3, \tag{13}$$

where the term proportional to T is contributed by the conduction electrons, and the second term by lattice vibrations at low temperatures, Θ_n being the Debye characteristic temperatures of the normal state.

In all calorimetric experiments on superconductors the electronic contribution to specific heat has been zero, while the Debye term remains but with a different value Θ_s of the characteristic temperature. Therefore $C_p(s)$ can be written

$$C_p(s)=464.4T^3/\Theta_s^3. \tag{14}$$

If Eqs. (12), (13), and (14) are combined it is seen that the value of the constant γ of the electronic specific heat term is

$$\gamma=0.0375,$$

and that

$$\Theta_s^{-3}-\Theta_n^{-3}=0.00150/464.4=3.24\times 10^{-6}.$$

The value of Θ_n can be estimated from Lindemann's empirical equation,[18]

$$\Theta=c(T_m/AV^{\frac{2}{3}})^{\frac{1}{2}}.$$

where A is the atomic weight, V the atomic volume (cm^3/mole), T_m the melting point in °K, and c a constant having values from 115 to 142 as determined from known Debye Θ values. Using $c=135$, $A=92.91$, $V=10.87$ cm^3/mole and $T_m=2415°\text{C}=2688°\text{K}$, the value of Θ_n for Cb is 330°K, so that $\Theta_n^{-3}=0.04\times 10^{-6}$, which leads to an estimate of Θ_s as $\sim$67°K.

The electronic specific heat of columbium calculated from $H-T$ measurements is higher than calorimetric values that have been observed in other transition metals. This, however, is not surprising in view of its observed magnetic behavior. The occurrence of large values of γ has been observed only in the "transition metals" in which the *d*-bands are partially filled, and this circumstance has been accounted for by extending the free electron theory of Sommerfeld by an appropriate quantum-mechanical treatment to include the effects of the nuclei and bound electrons on the conduction electrons, as well as interaction terms between the conduction electrons themselves. It is the latter type of interaction that has so far provided the best possibility of accounting for the larger values of γ although compensating effects and the extreme difficulty of the calculation make a detailed prediction impossible.[19]

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[18] Lindemann, Physik Zeits. **11**, 609 (1910).

[19] E. Wigner, Trans. Faraday Soc. **34**, 678 (1938).