Some Properties of Superconductors below 1°K. III. Zr, Hf, Cd, and Ti†

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Using techniques for the measurement of the magnetic threshold curves of superconductors below 1°K previously employed, investigations have been made on cadmium, zirconium, hafnium, and titanium, both before and after heat treatment. It was found that, in zirconium and hafnium, the magnetic superconducting properties were profoundly affected by heat treatment and that only after suitable annealing did these properties approach those of an ideal superconductor. The results for the annealed metals were as follows: the transition temperature, T_c, in zero magnetic field was 0.602°K for cadmium, 0.546°K for zirconium, 0.374°K for hafnium, 0.558°K for titanium and the slope of the magnetic threshold curves at $T=T_c$ in gauss/degree was 112 for cadmium, 170 for zirconium, 230 for hafnium, and 450 for titanium. The magnetic threshold curves for cadmium and zirconium were parabolic with $H_0=33.8$ gauss for cadmium and 46.4 gauss for zirconium. The thermodynamically computed specific heat of the normal electrons was $1.54\times10^{-4}T$ cal/mole-deg for cadmium and $3.92\times10^{-4}T$ mole-deg for zirconium. No thermodynamic computations were made for hafnium and titanium owing to the irreversibility of their superconducting transitions.

1. INTRODUCTION

IN continuation of measurements reported previously by Daunt and Heer[1,2] on the magnetic properties of superconductors below 1°K, we have extended the observations to other materials which only recently have been available to us in high purity. These measurements, carried out in the region obtainable by magnetic cooling methods, have enabled the specific heat of the electron assemblies in the normal state to be computed as has previously been done for superconductors in the helium region by Daunt and Mendelssohn.[3] They have led also to interesting results on the influence of physical strain on the magnetic properties of superconductors. The three metals, zirconium, hafnium, and titanium, are not only difficult to obtain in a strain-free state, because of their hardness, but also they all show a crystallographic modification from hcp to bcc at high temperatures, which makes heat treatment more complex than in many other superconductive metals. In our measurements, therefore, the influence of metallurgical properties of heat treatment has been considered, as is reported below. In the case of zirconium, it appears that after careful heat treatment, we have obtained a material which approaches the behavior of an "ideal" superconductor.

TABLE I. Physical properties of metals used.

Metal	Melting temp., °C	Recrystallization temp., °C	Transformation temp., °C (hcp to bcc)	Minimum hardness known (Rockwell scale)
Cd	321	about room temperature		$H47$
Zr	1865	~500	862	$E58$[c]
Hf[a]	2130	~800	1310	$B88$
Ti[b]	1800	~600	882	$B22$[d]

[a] See reference 6.
[b] See, for example, *Handbook on Ti-metal* (Titanium Metals Corporation, 1950).
[c] Our measurements on the zirconium listed in Sec. 5(b) of this paper.
[d] Our measurements on high purity titanium type No. 203-8 supplied by Foote Mineral Company.

2. THE EXPERIMENTAL ARRANGEMENTS

Temperatures below 1°K were produced by the magnetic cooling method. The paramagnetic salt used as the cooling substance in all experiments was chromium potassium alum. The superconducting metal to be investigated was pressed inside a "pill" composed of the metal and the powdered salt, and, as previously reported,[2,4] good thermal contact with the working substance was thereby obtained. Full details of our experimental arrangements and methods have been given previously by Daunt and Heer.[2] The temperature for transition from the superconducting to the normal state of the metal was observed, either in zero magnetic field or in an applied exterior magnetic field. The observation was made by measuring the magnetic susceptibility changes occurring in the "pill" as the temperature increased with time from a low temperature up to 1°K. The magnetic changes that occur in the metal at the transition are described fully in a previous paper.[2] By measuring the transition temperature as a function of the exterior field, the magnetic threshold curve is obtained for each metal, this magnetic threshold curve being in the nature of a phase diagram for the superconductor.

3. THE PROPERTIES OF THE SPECIMENS

In Table I, the relevant physical properties of the metals used in these investigations are set out. From this table, the appropriate annealing temperatures may be obtained, being between the recrystallization temperatures and the transformation temperatures.

† Assisted by a contract between the AEC and The Ohio State University Research Foundation.
[1] J. G. Daunt and C. V. Heer, Phys. Rev. **76**, 715 (1949).
[2] J. G. Daunt and C. V. Heer, Phys. Rev. **76**, 1324 (1949).
[3] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. (London) **A160**, 127 (1937). See also Daunt, Horseman, and Mendelssohn, Phil. Mag. **27**, 754 (1939).
[4] N. Kurti and F. Simon, Proc. Roy. Soc. (London) **A151**, 610 (1935).

In preparing the specimens, the metal was placed inside a pill of powdered chromium potassium alum which was pressed to 5000 lb/in.[2] and then formed to an ellipsoidal shape. The dimensions of the metal specimens and of the final pills are given in Table II.

In computing the temperature, T_s^*, on the Curie scale for a spherically-shaped specimen, it is necessary to correct the observed T^* for the shape and filling factor of the salt. Details of the method of making these corrections are given elsewhere,[2,5] which involve the parameters f and Δ, where the salt filling factor f is defined by the ratio of the distributed density of the powdered salt to the crystalline density, and where Δ is defined by

$$\Delta = cf(4\pi/3 - N),$$

where c is the Curie constant per cc of the salt and N the demagnetization factor of the specimen. The values of f and Δ for each specimen are given in Table II.

TABLE II. Heat treatment, physical properties, and dimensions of specimens.

Specimen[a]	Heat treatment	Hardness, Rockwell scale	Dimensions of metal (mm)	Axes of ellipsoidal salt pill (mm)	f	Δ
Cd	Annealed at 150°C for 1.5 hours.		Ellipsoid with axes 19×6	36×13	0.81	0.022
Zr(U)	Unannealed	*E*61	11×5.5×3.3	39×12.7	0.90	0.017
Zr(A)	Annealed at 800°C for 2.5 hours.	*E*58	11×5.5×3.3	35×12.7	0.94	0.026
Hf(U)	Unannealed	*C*47	Cylindrical 50.5 long ×3.4 diam	29×12.7	0.98	0.015
Hf(A)	Annealed at 900°C for 3 hours.	*B*100	Cylindrical 50.5 long ×3.4 diam	19×13	0.92	0.007
Ti[b](U)	Unannealed	*B*32	Irregular pieces 2–3 mm	27×13	0.79	0.011
Ti(A)	Annealed at 800°C for 2.5 hours	*B*28	Irregular pieces 2–3 mm	22×12.7	0.94	0.011

[a] The suffixes (U) and (A) indicate the unannealed and the annealed specimens, respectively.
[b] See reference 1.

The sources and purities of the metals used were as follows: (a) cadmium: obtained from Johnson Matthey and Company, Lab. No. 2572, purity 99.99 percent: (b) zirconium: kindly loaned by Oak Ridge National Laboratory. The metal used was cut from a crystal bar formed by deposition from the iodide and was of purity 99.9 percent. The greatest single impurity was 0.04 percent by weight hafnium; (c) hafnium: kindly loaned by the U.S.A.F. Institute of Technology, Dayton, Ohio, and originally prepared by the Foote Mineral Co. It was Hf "783" (see paper by Litton[6]) of purity 98.92 percent, having approximately 0.9 percent zirconium impurity and was prepared by deposition from the iodide. It was in the form of a swaged rod; (d) titanium: This was the same as that previously used by Daunt and Heer[1] in their magnetic measurements. This specimen was kindly loaned by the Battelle Memorial Institute, Columbus, Ohio, and was prepared by deposition from the iodide.[7] Its purity was 99.95 percent.

The superconducting properties of zirconium, haf-

TABLE III. Magnetic threshold values for the superconducting transition. Temperature is expressed on Curie scale, T_s^*, which approximates within experimental error the absolute temperature T°K. The suffixes (A) and (U) refer to the metals in the annealed and unannealed states, respectively.

Cd		Zr(A)		Hf(A)		Ti(A)	
T_s^*	H(gauss)	T_s^*	H(gauss)	T_s^*	H(gauss)	T_s^*	H(gauss)
0.602	0.0	0.546	0.0	0.383	0.0	0.558	0.0
0.560	6.03	0.516	5.93	0.372	0.0	0.527	10.4
0.502	9.95	0.516	6.93	0.367	0.0	0.491	20.8
0.490	11.0	0.464	11.0	0.327	6.6	0.444	36.4
0.428	16.5	0.436	16.5	0.340	11.0	0.436	51.0
0.408	18.7	0.382	22.0	0.312	16.5	0.408	62.3
0.359	22.0	0.314	23.0			0.408	78.0
0.326	23.1					0.395	88.5
0.264	27.5					0.334	104.0
		Zr(U)		Hf(U)		Ti(U)	
		0.565	0.0	No observable evidence of superconductivity.		0.523	0.0
		0.375	63.0			0.528	0.0
		0.325	83.5			0.517	8.0
						0.512	11.0
						0.487	16.3
						0.483	21.6
						0.447	27.2
						0.437	30.7
						0.410	36.0
						0.384	44.3
						0.360	50.3
						0.335	54.7
						0.325	57.4

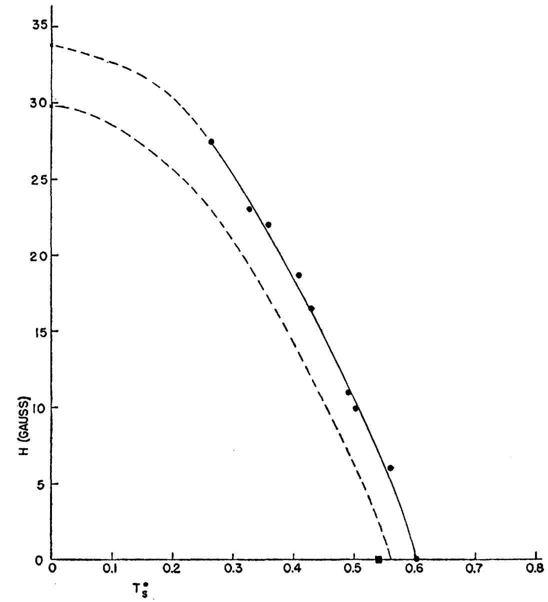

FIG. 1. Magnetic threshold curve for cadmium. ●—our results; - - - curve obtained by Goodman and Mendoza;[11] ■—result of Kurti and Simon. (See reference 4.)

[5] N. Kurti and F. Simon, Phil. Mag. 26, 849 (1938).
[6] F. B. Litton, J. Electrochem. Soc. 98, 488 (1951).
[7] Campbell, Jaffee, Blocher, Gurland, and Gonser, J. Electrochem. Soc. 93, 271 (1948).

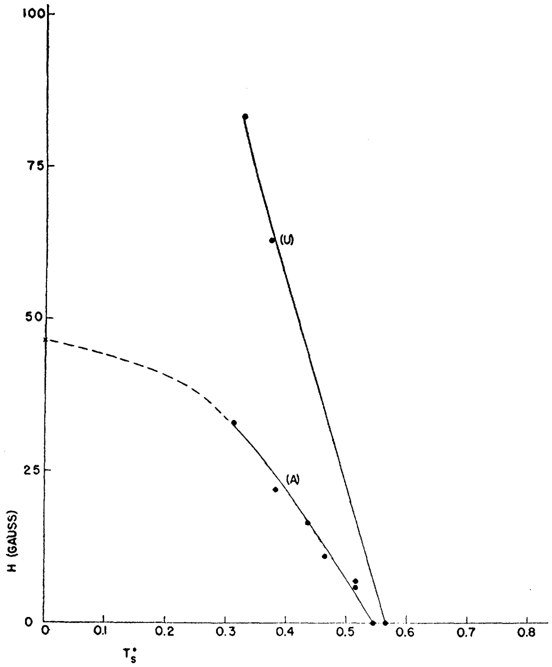

FIG. 2. Magnetic threshold curve for zirconium. Curve (U) is for unannealed zirconium; curve (A) for the annealed zirconium.

nium, and titanium were investigated both before and after vacuum annealing. For the cadmium, measurements were made only after annealing. The temperatures and duration of the annealing processes for each specimen are recorded in Table II. In each case the temperature was reduced slowly after the completion of the anneal. The hardness of the metals both before and after annealing was measured using a Tukon hardness testing machine for the hafnium and a Rockwell hardness machine for the titanium and zirconium, and is also recorded in Table II.

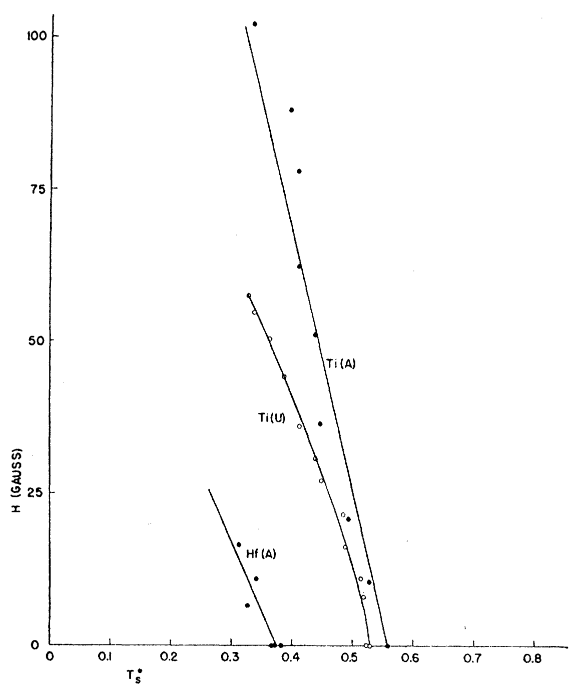

FIG. 3. Magnetic threshold curves for partially annealed titanium—Ti(A); unannealed titanium—Ti(U); and partially annealed hafnium—Hf(A).

4. THE RESULTS

The observed temperatures of the superconducting transition in zero field and in applied magnetic fields are tabulated in Table III and are shown in Figs. 1–3. The temperatures are expressed on the Curie scale, T_s^*, corrected to a spherically-shaped salt specimen. In the region of measurement the difference between T_s^* and the bsolute temperature T°K is estimated[8] to be within the experimental error.

For cadmium it was found that the results for the magnetic threshold curve could be expressed adequately by the parabolic formula:

$$H=H_0[1-(T/T_c)^2], \tag{1}$$

with H_0, the threshold field at $T=0$, equal to 33.8 gauss and T_c, the transition temperature in zero field, equal to 0.602°.

For zirconium it was found that the annealing made profound changes. Unannealed zirconium, Zr(U), gave $T_c=0.565°$ and the slope of the threshold field at T_c, namely $(\partial H/\partial T)_{T=T_c}$ equal to 335 gauss/degree. After annealing the zirconium, Zr(A), was found to show a parabolic threshold curve having $H_0=46.6$ gauss and $T_c=0.546°$. The reduction in the threshold field after the anneal was noteworthy,[9] as is shown in Fig. 2.

The unannealed hafnium, Hf(U), showed no magnetically observable sign of superconductivity down to 0.15°K. The annealed hafnium, Hf(A), was, however, found superconductive with $T_c=0.374\pm0.01$ and $(\partial H/\partial T)_{T=T_c}$ approximately equal to 230 gauss/degree.

The measurements on titanium showed little difference between the results for the annealed, Ti(A), and the unannealed, Ti(U), samples.

The relevant data are collected together in Table IV, along with the normal electronic specific heats which can be calculated thermodynamically from them.

5. DISCUSSION OF THE RESULTS AND THE THERMODYNAMIC DATA DEDUCIBLE THEREFROM

(a) Cadmium

Since a few measurements have been made previously of the threshold curve of cadmium,[4,10,11] our measurements were carried out largely in order to check the reproducibility of our technique. The previous results are indicated in Fig. 1 along with our present results.

[8] M. H. Hebb and E. M. Purcell, J. Chem. Phys. **5**, 388 (1937).
[9] A brief abstract of these results is given by T. S. Smith and J. G. Daunt, Phys. Rev. **86**, 818 (1952).
[10] J. G. Daunt, unpublished.
[11] B. B. Goodman and E. Mendoza, Phil. Mag. **42**, 594 (1951).

It will be seen that our value for the transition, T_c, in zero field is 0.602°K as compared with 0.560°K of Goodman and Mendoza[11] and 0.54°K of previous work.[4,10] Moreover, the threshold curve we observed is about 5 gauss higher than that given by Goodman and Mendoza.[11] This may be due to the difference in the materials used, the latter authors employing cadmium from the New Jersey Zinc Company of estimated purity 99.996 percent. Some confirmation of this conclusion comes from recent measurements by Steele[12] also on Johnson Matthey cadmium, who found $T_c = 0.650$ and a threshold curve in fair agreement with that reported here.

For a superconductor having a parabolic magnetic threshold curve, which marks the *reversible* boundary between the superconductive and the normal states, the specific heat of the normal electrons, $C_{el,\,n} = \gamma T$, can be calculated thermodynamically, as has been done previously,[3,13,14] and is given by

$$C_{el,\,n}/T = \gamma = (V/8\pi)(\partial H/\partial T)^2{}_{T=T_c}, \qquad (2)$$

where V is the atomic volume of the metal. Our results for cadmium lead to $\gamma = 1.54\times10^{-4}$ cal/mole-degree,[2] as compared with 1.28×10^{-4} cal/mole-degree[2] which was computed from the results of Goodman and Mendoza.[11]

(b) Zirconium

Our results for annealed zirconium, Zr(A), give threshold field values and transition temperatures lower than both the values of the unannealed, Zr(U), and the values obtained previously.[4,10] Indeed, it is noteworthy that our results for the unannealed Zr(U) of $T_c = 0.565$°K and $(\partial H/\partial T)_{T=T_c}$ equals 335 gauss/degree approximate closely those previously measured by Kurti and Simon,[4] of $T_c = 0.68$°K and $(\partial H/\partial T)_{T=T_c}$ equal 400 gauss/degree, and by Daunt,[10] of $T_c = 0.60$°K and $(\partial H/\partial T)_{T=T_c}$ equal 375 gauss/degree. It is concluded that the previous workers did not undertake heat treatment of their samples. The relatively low value of $(\partial H/\partial T)_{T=T_c}$ observed by us for the annealed Zr(A) indicates that annealing of the specimen produces a superconductor for which the magnetic transition approximates a reversible process and for which the magnetic threshold curve becomes parabolic. A similar approach of the behavior of superconductors to that of the "ideal" superconductor showing a reversible Meissner[15] effect on careful heat treatment has been observed previously for thorium by Shoenberg[16] and for vanadium by Wexler and Corak.[17] In the case of metals such as zirconium, hafnium, and titanium, however, all of which show an α- to β-phase transformation at elevated temperatures, it is not clear whether the approach to ideality in the superconductive behavior on heat treatment is due to the annealing out of strains in the lattice or is due, at least partly, to the removal by heat treatment of inclusions of metastable β-phase. It is well known from the work of Lazarew and Galkin[18] and of Khotkevich and Golik,[19] as well as that of Wexler and Corak,[17] that physical strain produces marked irreversibilities in the superconductive transition, as well as changes in the transition temperature T_c, and it would be possible to explain the effects of heat treatment on the basis of strain annealing. On the other hand, the following facts in the case of our measurements on zirconium are of interest. (a) There was little change in measured hardness by the anneal; the hardness, in fact, changing from Rockwell *E*61 to *E*58 (see Table II). This indicates that there was no great strain condition before the heat treatment. (b) If it is assumed that our results for the magnetic threshold curve represent a reversible transition curve, then using formula (2) we deduce that the normal electronic specific heat parameter $\gamma = 3.92\times10^{-4}$ cal/mole-degree.[2] This is to be compared with the result obtained calorimetrically by Friedberg, Estermann and Goldman[20] of $\gamma = 6.92\times10^{-4}$ cal/mole-degree[2] on a non-heat-treated sample. This discrepancy cannot be explained by a complete inapplicability of the assumption made above of reversibility of the magnetic transition, since irreversibilities tend to increase the thermodynamically computed γ-values. The discrepancy, therefore, is probably real. This discrepancy, together with the marked changes we observed in the superconducting behavior through heat-treatment, may be due to inclusions of metastable β-phase zirconium in samples that have not been heat treated. Calorimetric measurements also on carefully annealed zirconium, therefore, would be of interest.

TABLE IV. The observed properties of cadmium, zirconium, hafnium, and titanium.

Metal	T_c °K	H_0 gauss	$(\partial H/\partial T)_{T=T_c}$ gauss/deg	γ[a] cal/mole-deg²	γ/V[b] cal/cc-deg²
Cd	0.602	33.8	112	1.54×10^{-4}	1.18×10^{-5}
Zr(U)	0.565	···	335	···	···
Zr(A)	0.546	46.6	170	3.92×10^{-4}	2.76×10^{-5}
Hf(U)	No magnetically observable evidence of superconductivity.				
Hf(A)	0.374	···	230	···	···
Ti(U)[c]	0.53	···	470	···	···
Ti(A)	0.558	···	450	···	···

[a] The normal electronic specific heat $C_{el,n} = \gamma T$.
[b] V is the atomic volume. This column is included for reference to the correlation among superconductors proposed by one of us [see J. G. Daunt, Phys. Rev. 80, 911 (1950); and J. G. Daunt and T. S. Smith, Phys. Rev. 88, 309 (1952)].
[c] Data from Daunt and Heer (reference 1).

[12] M. C. Steele and R. A. Hein, Phys. Rev. **87**, 908 (1952).
[13] J. A. Kok, Physica **1**, 1103 (1934).
[14] J. G. Daunt, Phys. Rev. **80**, 911 (1950).
[15] W. Meissner and R. Ochsenfeld, Nature **21**, 787 (1933).
[16] D. Shoenberg, Proc. Cambridge Phil. Soc. **36**, 84 (1940).
[17] A. Wexler and W. S. Corak, Phys. Rev. **85**, 85 (1951).
[18] B. G. Lazarew and A. Galkin, J. Phys. (U.S.S.R.) **8**, 371 (1944).
[19] V. Khotkevich and V. R. Golik, J. Theor. Exp. Phys. (U.S.S.R.) **20**, 427 (1950).
[20] Friedberg, Estermann, and Goldman, Phys. Rev. **85**, 375 (1952).

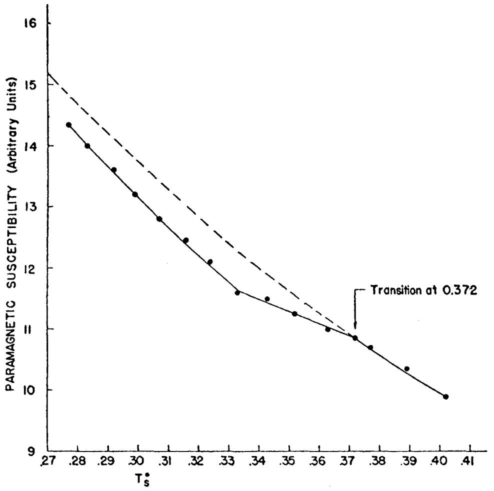

FIG. 4. Warm-up curve, in zero magnetic field, of chromium potassium alum and hafnium (A).

(c) Hafnium

The results given in Sec. 4 above for hafnium were found to be very strongly dependent on the method of preparation of the specimen. Before the annealing process above, the specimen was very hard (about Rockwell C47) and at low temperatures down to 0.15°K showed no sign of superconductivity. After the anneal, although evidence of superconductivity was observed, the transition did not correspond to zero magnetic induction over the entire volume of the specimen, as is shown by the curve of Fig. 4 which gives the susceptibility of the sample of metal and salt in zero magnetic field *versus* temperature; whereas for zirconium, titanium, and cadmium the measured magnetic induction corresponded to 100 percent of the volume of the metal becoming superconductive at the transition. Evidently, in hafnium the lack of 100 percent superconductivity and the irreversibility of the Meissner effect are due to extreme hardness of the samples. It is to be noted that even after our heat treatment the hafnium sample had a measured hardness of Rockwell $B100$, which, as is shown in Table II, is very considerably harder than the zirconium and titanium we employed. In consequence, no computations are made from our results of the γ-value for hafnium, since it is unlikely that the observed threshold curve represents a reversible transition. Moreover, since the hardness of our specimen, even after the anneal, was still somewhat greater than that quoted by Litton,[6] it is possible that a softer specimen would show 100 percent superconductivity by volume. Our value of $T_c=0.37$°K is to be compared with $T_c=0.35$°K given by Kurti and Simon.[4] It is possible that a softer specimen of hafnium may show a transition temperature, T_c, considerably smaller than that quoted here.[21] Our observations on the hafnium transition in a magnetic field did not have the same accuracy as those obtained for zirconium and titanium, as can be deduced from the scatter of the points. This was due to the fact that apparently only part of the volume underwent transition.

For a metal having such a low value of T_c, the slope of the magnetic threshold curve of $(\partial H/\partial T)_{T=T_c}$ equals 230 gauss/degree is very high (see reference 14), a result which is in line with the observed non-ideal behavior of the transition.

(d) Titanium

The observations on the titanium specimen were carried out in order to see whether the heat treatment altered the evaluations of T_c and $(\partial H/\partial T)_{T=T_c}$ previously observed by Daunt and Heer[1] on the same (untreated) specimen. The measured hardness before the heat treatment was Rockwell $B32$, whereas after the anneal at 800°C it was $B28$. The difference, therefore, was not great, and, as was expected, the observed values of $T_c=0.558$°K and $(\partial H/\partial T)_{T=T_c}$ equals 450 gauss/degree were practically identical with those previously observed, namely $T_c=0.53$°K and $(\partial H/\partial T)_{T=T_c}$ equals 470 gauss/degree. Evidently, the titanium, even after this heat treatment, still showed a highly irreversible superconductive transition, and for this reason no thermodynamic computations have been made from our results.

We wish to thank the Research Corporation for a grant which has greatly aided this research.

[21] *Note added in proof:* For example, a value of $T_c=0.30$°K for an annealed Hf sample (containing 10 percent Zr) has been reported by L. D. Roberts (1952 New York Meeting of the American Physical Society).