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Superconductivity of Vanadium*

AARON WEXLER AND WILLIAM S. CORAK
Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania

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The presence of small quantities of oxygen and nitrogen in interstitial positions in the vanadium lattice is found to affect markedly the superconductive properties of the metal. X-ray evidence supports the supposition that these impurities set up internal strains which are known to give rise to properties very similar to those of the hard superconductors. It is suggested that these strains, which, unlike those arising from mechanical work, are not always removable by vacuum heat treatment, are responsible for the difficulties associated with the preparation of samples of the metals exhibiting a reversible B, H curve.

It is shown that the sharp penetration fields for a relatively pure specimen are probably not very different from the equilibrium fields. The transition temperature of vanadium is 5.13°K, $(dH_c/dT)_{T_c}=436\pm20$ oersteds/deg, and the Sommerfeld $\gamma=15\times10^{-4}$ cal/mole deg K^2.

I. INTRODUCTION

THE superconductivity of vanadium is of interest because this metal is one of the so-called hard superconductors whose superconductive properties are highly dependent on the physical and chemical state of the metals. Most specimens of the hard superconductors, which are uranium and the metals of the fourth and fifth transition groups of the periodic table, exhibit appreciable hysteresis in their isothermal B, H curves and three progressively steeper H_c, T curves depending upon whether these are obtained by measurements of critical currents, the magnetic fields which will first penetrate the metal, or the magnetic fields which completely restore normal resistance. In addition, the transition between the superconductive and normal states is not sharp. In contrast with these properties, the mechanically soft metals of the second, third, and fourth groups have practically reversible B, H curves, sharp transitions, and their H_c, T curves are independent of the method of measurement. The work on vanadium reported here is part of a program designed to determine the factors and the mechanisms which are responsible for the properties of the hard superconductors; other superconductors in this classification are also under investigation. Attention to previous work on the hard superconductors titanium,[1] zirconium,[2] hafnium,[2] thorium,[3] vanadium,[4] niobium,[5,6] tantalum,[7] and uranium,[8] may best be drawn by indicating the most recent pertinent papers wherein detailed references to previous work may be found.

The work reported here, when correlated with the results of the investigations of others, indicates that the properties of the hard superconductors outlined above arise from inhomogeneous strains which may be set up in the lattice either by mechanical work or by impurities, particularly carbon, oxygen, and nitrogen, which at low concentrations are known to enter the lattice interstitially. The most striking differences in physical properties between the soft and hard superconductors are the much higher cohesive strengths and mechanical hardness of the latter group. For the purpose of this discussion, the most important corollary of the first factor is the high recrystallization temperatures[9] of hard superconductors. Thus while mechanically produced strains in the soft superconductors are easily removed by an annealing operation (indeed, most of these metals self-anneal at room temperature), quite high temperatures are required for the transition metals. The hardness of these metals increases strongly with mechanical work and especially with increasing content of carbon, nitrogen, and oxygen. From thermodynamic considerations it can be shown[10] that the removal of these contaminants by high vacuum heat treatment is most difficult and, in fact, particularly in the case of oxygen such treatment may increase their concentration through the reaction of the metal with the residual gases in the vacuum. In connection with attempts to remove such contaminants, it is therefore necessary to consider the thermodynamics and kinetics of the reactions involved. This, however, is made difficult by the paucity of data for the thermodynamic stability of alloys containing only a very small fraction of an atomic percent of the interstitial solutes.[11] Metallurgists[12,13] have used the hardness of annealed metals of the fourth, fifth, and sixth transition groups as an index of their content of interstitially located impurities. It seems reasonable to use this same property as a criterion of

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

[2] N. Kurti and F. Simon, Proc. Roy. Soc. (London) **A151**, 610 (1935).

[3] D. Shoenberg, Proc. Cambridge Phil. Soc. **36**, 84 (1940).

[4] A. Wexler and W. S. Corak, Phys. Rev. **79**, 737 (1950).

[5] Cook, Zemansky, and Boorse, Phys. Rev. **80**, 737 (1950).

[6] L. C. Jackson and H. Preston-Thomas, Phil. Mag. **41**, 1284 (1950).

[7] R. T. Webber, Phys. Rev. **72**, 1241 (1947).

[8] B. B. Goodman and D. Shoenberg, Nature **165**, 441 (1950).

[9] F. Seitz, *The Physics of Metals* (McGraw-Hill Book Company, Inc., New York, 1943), Chapter IV.

[10] E. A. Gulbransen and K. F. Andrew, J. Electrochem. Soc. **97**, 396 (1950).

[11] See for example, O. Kubaschewski and E. V. Evans, *Metallurgical Thermochemistry* (Butterworth-Springer, Ltd., London, 1950), pp. 63–65.

[12] A. E. van Arkel, *Reine Metalle* (Julius Springer, Berlin, 1939).

[13] R. I. Jaffee and I. E. Campbell, Trans. Am. Inst. Mech. Engrs. **185**, 646 (1949).

TABLE I. Characteristics of the vanadium samples.

Sample	Length (cm)	Diameter (cm)	Hardness[a] kg/mm²	Residual[c] resistance ratio	Weight % of non-metal impurities		Source
					Oxygen	Nitrogen	
A	2.54	0.55 (max)[b]	65±10	···	0.038	0.021	Battelle Memorial Institute
B	2.54	0.178	···	0.051	···	···	Battelle Memorial Institute
C	2.22	0.357	113±5	0.069	0.044	0.032	General Electric Company
D	2.54	0.278	185±5	0.173	0.075	0.106	Union Carbide and Carbon Corporation
E	2.54	0.276	343±10	0.259	0.15	0.189	Westinghouse Electric Corporation

[a] These measurements all refer to a 1 kg load and were made with a "Tukon" tester, a description of which may be found in *Metals Handbook* (Am. Soc. Metals, Cleveland, Ohio, 1948), pp. 93–105.

[b] The maximum diameter only is noted to give an idea of the size of the specimen, which, consisting of a large number of individual crystals bonded together at isolated points, was necessarily irregular.

[c] The residual resistivity, obtained at 4.90°K by quenching superconductivity with an external magnetic field, relative to the ice point resistivity.

the severity of internal strains. To paraphrase the foregoing, it should be pointed out that in the case of the transition metals which readily accommodate carbon, nitrogen, and oxygen in the interstices between the metal atoms, simple vacuum heat treatment can only remove the internal strains due to cold work but not, in general, those due to the interstitially located foreign atoms which are stable at elevated temperatures. Thus the hardness increment due to increased content of these interstitial impurities is essentially unaffected by simple annealing.

Now it is known[14] that tension applied to a superconductor raises and compression lowers its transition temperature. It has also been shown[15] most clearly that a superconductor inhomogeneously strained by the application of external forces acquires abnormal properties including those which characterize most samples of the hard superconductors. Hence it is clear that mechanical strains and especially interstitially located foreign atoms may be responsible for the departure of the hard superconductors from simple, ideal behavior.

If, indeed, interstitially located atoms are largely responsible for internal strains which confer the characteristic properties of the hard superconductors, then their effect would depend on the crystal structures and atomic volumes of the metals. Supporting evidence for these ideas may be found in the following: The metals of the fifth transition group, V, Nb, and Ta have body-centered cubic structures while of those of the fourth group Ti, Zr, and Hf have hexagonal close-packed structures and Th is face-centered cubic. Thus for a given atomic volume, the largest interstices will be found in the metals of the fourth transition group, and this fact, coupled with the larger atomic volumes of these metals, indicates that the metals of the fourth group should be less affected by interstitial impurities than those of the fifth group. In the light of these remarks, the extreme cases vanadium and thorium may be considered. The room temperature atomic volume of vanadium is 0.42 that of thorium. It is known that mechanically soft thorium is not difficult to prepare and that its hardness is much less affected by nitrogen and oxygen than is that of vanadium, whose hardness is very markedly increased by oxygen and nitrogen absorption. It is therefore significant to note that the only sample of a transition metal superconductor which has been found to display a completely ideal *B*, *H* curve was one of thorium[3] prepared by the thermal decomposition of its iodide,[16] a process which is known to produce a very soft product most free of interstitial impurities.[12] Another sample of thorium[3] investigated by Shoenberg, which showed the properties typical of hard superconductors, was prepared by calcium reduction of the

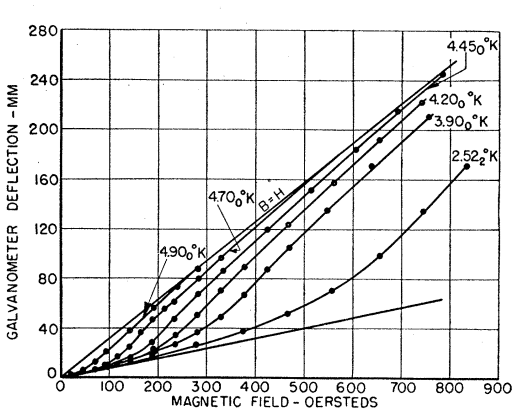

FIG. 1. Magnetic induction in specimen *A*.

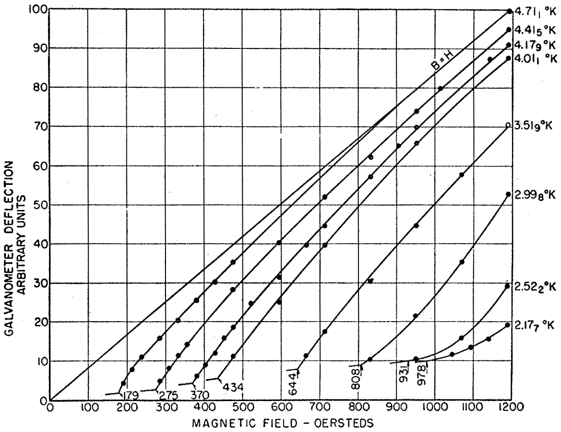

FIG. 2. Magnetic induction in specimen *B*.

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[14] C. J. Sizoo and H. Kamerlingh Onnes, Leiden Commun. 180b.

[15] B. Lasarew and A. Galkin, J. Phys. (U.S.S.R.) **8**, 371 (1944).

[16] Private communication from Dr. Shoenberg.

oxide followed by powder metallurgy. This method is known[12] to produce a harder material corresponding to a higher nitrogen, oxygen content. The most extreme case of departure from ideal superconductive behavior was obtained for a very hard sample of vanadium,[17] which gave a $(dH_c/dT)_{T_c}$ of about 4000 oersteds/deg, where H_c is essentially the field at which normal resistance was restored.

The present investigation was undertaken to determine the role of internal strains due to oxygen and nitrogen, as reflected in the mechanical hardness of the metal. It was a further purpose of the work to ascertain the physical significance of the various values of $(dH_c/dT)_{T_c}$ obtained for hard superconductors and in particular to obtain an estimate of this quantity corresponding to that which would be characteristic of a sample exhibiting thermodynamic reversibility in the superconductive transition.

II. CHARACTERISTICS OF THE SPECIMENS STUDIED

The magnetic properties of five specimens of vanadium, obtained from various sources and described in Table I, were investigated. Spectrographic analysis of these materials indicated rather similar contents of other metals. The major metallic impurity is less than 0.1 percent iron, while the sum of other metallic impurities is of the order of 0.1 percent. The major differences among the samples are in the nitrogen, oxygen content, and this is seen to be reflected in a rather large range of hardness increasing monotonically with the concentrations of these impurities.

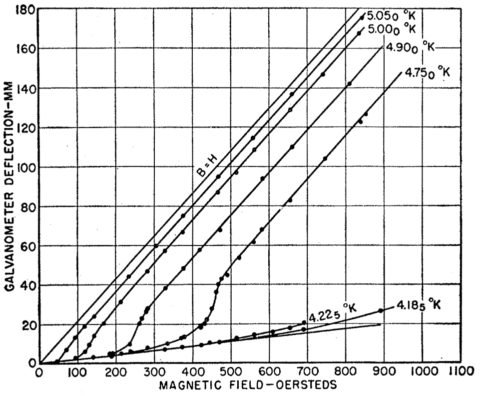

FIG. 3. Magnetic induction in specimen C.

Van Arkel[12] has described the various modes of preparation of vanadium. Sample A was grown by the thermal decomposition of vanadium diiodide on a three-mil diameter tungsten filament. The sample consisted of crystals of linear dimensions of the order of 1 mm, the contact between the individual crystals being mechanically weak because of voids. In order to minimize the shape demagnetization effects of such an array of crystals, this material was swaged down to give a uniform mass from which sample B was carefully machined. Sample C was obtained from some vanadium prepared by calcium reduction of the pentaoxide. In this particular preparation, the reaction temperature exceeded the melting point which resulted in a melted specimen from which sample C was machined. Sample D was obtained in a manner similar to that just described; in addition, however, the specimen from which the sample was machined was remelted in a pure argon atmosphere. Sample E resulted from the sintering by heat and pressure of fine particles of vanadium prepared by the calcium reduction method. Because of the nature of their preparations, samples A, C, and D were probably free of mechanical strains. Sample E was subjected to a high vacuum anneal at 800°C.

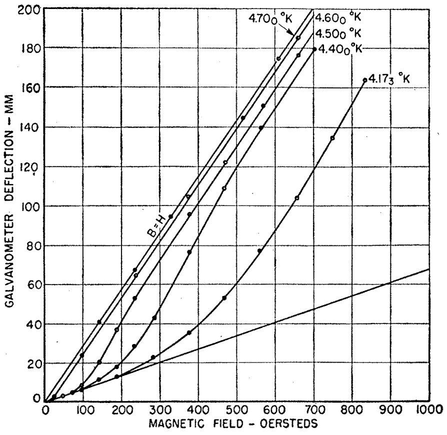

FIG. 4. Magnetic induction in specimen D.

The grain sizes of the specimens were determined by metallographic examination. The grain sizes of C were in the range 0.2–1 mm; those of D were slightly larger. In both cases, the crystal boundaries were almost straight lines and were well defined. The grains of E were smaller by about an order of magnitude, and the

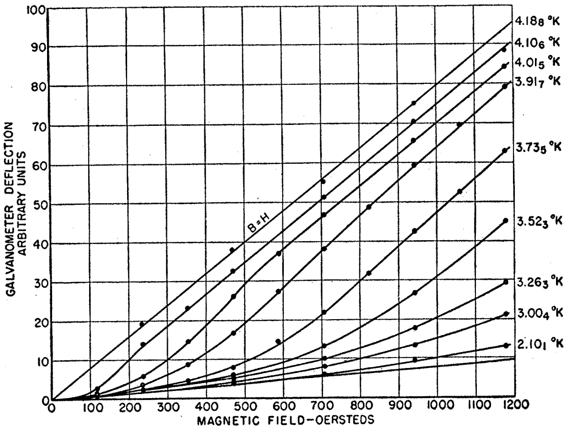

FIG. 5. Magnetic induction in specimen E.

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

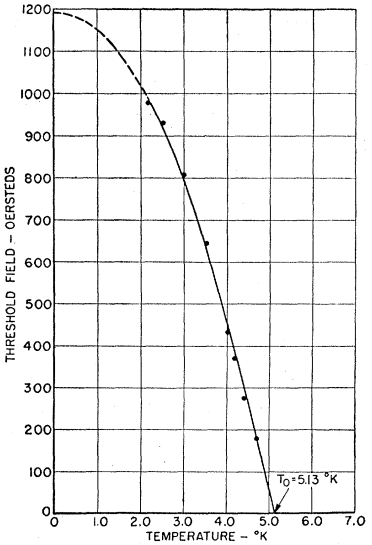

FIG. 6. Threshold fields for superconductive vanadium.

crystal boundaries were very irregular, as would be expected from the method of preparation.

The samples were also studied by x-rays, and all showed the body centered cubic structure. Specimen A was found to consist of relatively large single crystals, and the lattice parameter $a_0 = 3.0282 \pm 0.0001$A was determined at 30°C. For this material the diffracted beam was very sharp, indicating an unstressed lattice of uniform lattice spacings. As the nitrogen and oxygen content is increased, progressive line broadening is observed, indicative of a stressed lattice, and the lattice parameter increases to 3.0313 ± 0.0006A for C, 3.034 ± 0.001A for D, and 3.038 ± 0.002A for E. These results may account for the diversity of lattice parameters of vanadium recorded in the literature.[12] A similar correlation of lattice parameter and hardness with oxygen and nitrogen content at comparably low concentrations has been reported recently for titanium.[18,19]

III. MEASUREMENTS AND RESULTS

For the study of the magnetic properties of the specimens, the method of Keeley and Mendelssohn[20] was adopted because of its simplicity. A coil of No. 40 copper wire was wrapped around the specimens and, at various constant temperatures,[21] the deflection of the ballistic galvanometer to which the coil was connected was measured when a uniform magnetic field, longitudinally applied to the specimen, was reduced to zero. Applied to a specimen of pure tin (Johnson, Matthey, and Company Lab. No. 2356) of about the same dimensions as the vanadium specimens and machined in the same way, this procedure yielded data of the expected form. A plot of galvanometer deflection *vs* applied field consisted of three straight lines, showing that the magnetic induction B was zero for fields up to the critical field, H_c, i.e., $B=0$ for $0<H<H_c$. In a small field range of the order of 1 percent of H_c, B rose linearly to $B=H$. Above H_c the remanent B was 10 percent H_c when $H=0$, and this accounted for the displacement of the final portion of the curve from the $B=H$ line. The magnetic field was homogeneous and known to ±1 percent. Within these limits, the observed critical field agreed with the data of other workers.[22]

The results for the specimens listed in Table I are shown in Figs. 1–5 in the same sequence as they are tabulated. It was suspected that the fact that the initial field penetration of A (Fig. 1) was gradual might have been caused by the demagnetization effects of the irregularly shaped crystals which were bonded together at isolated points. This is confirmed in Fig. 2 which shows that the swaged sample, which was a smooth cylinder, exhibited sharp field penetrations, indicating that the superconductivity of a substantial fraction of the material was destroyed at well-defined magnetic fields. At temperatures near the transition temperature T_c, as the field increased above the penetration field the magnetic induction gradually rose to $B=H$ with no remanent flux when H was reduced to zero. This particular feature has not been observed before and may be connected with the fact that in these specimens the individual crystals were not bonded together on an atomic scale, as is the case with polycrystalline materials obtained from a melt. As would be expected of a material having a distribution of critical fields, as the temperature was lowered below T_c the fraction of the specimen whose superconductivity is destroyed by a small range of field ΔH above the penetration field H_c decreased and eventually the penetration became rather gradual. Arguments will be presented below supporting the hypothesis that the sharp penetration fields, plotted in Fig. 6, probably correspond closely to the equilibrium fields which would be evidenced by a pure, unstrained sample of the metal. The transition temperature may be obtained in several ways. The temperatures corresponding to $B=\frac{1}{2}H_c$ in Fig. 1 extrapolate to $T_c=5.13$°K when $H_c=0$. An identical value of T_c is obtained from the penetration fields for sample B as shown in Fig. 6.

The effect of increasing nitrogen and oxygen concentration can be seen in the curves for specimens C, D, and E. Thus for C the superconductivity of the specimen was destroyed gradually when the penetration field was exceeded. The penetration fields could be obtained if the sensitivity of the measurements was increased in the low deflection range. These data also yielded $T_c=5.13$° and $(dH_c/dT)_{T_c}$ was within 10 percent of the value obtained from the data for B. Again the decreasing

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[18] H. T. Clarke, Jr., Trans. Am. Inst. Mech. Engrs. **185**, 588 (1949).

[19] W. L. Finlay and John A. Snyder, Trans. Am. Inst. Mech. Engrs. **186**, 277 (1950).

[20] T. C. Keeley and K. Mendelssohn, Proc. Roy. Soc. (London) **A154**, 378 (1936).

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

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

slope with which the curve leaves the base line as the temperature is reduced is very evident. Still further increase in nitrogen and oxygen content lowered T_c and exaggerated the features outlined above, as shown in Figs. 4 and 5. For these specimens neither the penetration fields nor those corresponding to the completion of penetration could be obtained with any degree of reliability.

A comparison of our results with those of others,[17,23] on vanadium is somewhat difficult because earlier work was done by methods which essentially measure the resistance of the metals. The rather lower transition temperatures previously reported are probably due to the lower purity of the vanadium specimens used.

Recently questions have been raised[6] concerning the significance of the penetration fields and of the fields corresponding to the completion of penetration. If the characteristics of the hard superconductors are due to inhomogeneous internal strain, then it would appear that the initial sharp penetration fields corresponding to the destruction of superconductivity in an appreciable fraction of a given specimen would be close to the equilibrium fields of a pure specimen. The fact that the field continues to penetrate over a large range of H is expected in view of the internal strain. Confirmation of the significance of the penetration fields may be found in Shoenberg's work on thorium, which showed that the penetration fields of an impure sample were close to the equilibrium fields of a pure sample. While the best way to answer these questions would be to introduce nitrogen and oxygen into the lattice of a pure sample exhibiting a reversible B, H curve, the following arguments may illuminate the situation. It is well known[22,24,25] that the application of thermodynamics to the equilibrium threshold fields—temperature relation enables one to calculate the differences in thermal properties of the metal across the phase boundary. If additional assumptions are made, the thermal properties of the individual phases may be obtained. We are particularly interested in relating $(dH_c/dT)_{T_c}$ to a simple physical property of the metal so that the expected order of magnitude of this derivative may be estimated. For a specimen of zero demagnetization coefficient, the entropy difference is given by

$$\Delta S = S_s - S_n = (VH_c/4\pi)(dH_c/dT) \tag{1}$$

where V is the atomic volume, and the specific heat difference is

$$\Delta C = C_s - C_n = (VT/4\pi)[(dH_c/dT)^2 + (H_c d^2H_c/dT^2)]. \tag{2}$$

It has been pointed out[22] that if the linear term, T, of the specific heat of the normal phase is the Sommerfeld electronic term and if the specific heat of metal in the superconducting state does not contain a term linear in T, then

$$\gamma = (d\Delta S/dT)_{T=0} \tag{3}$$

which, by virtue of (1) may be derived from the equilibrium H_c *vs* T curve. It is to be noted that this method of determining γ involves a double differentiation. On the other hand, if, in addition to the assumptions already made, the following simple law is applicable

$$H_c = H_0[1 - (T/T_c)^2] \tag{4}$$

then it has been shown that

$$\gamma = (V/8\pi)(dH_c/dT)^2{}_{T_c} \tag{5}$$

which involves a single differentiation. Recently Goodman and Mendoza[26] showed that aluminum, cadmium, gallium, and zinc accurately obey Eq. (4) over the whole temperature range and hence used a relation equivalent to Eq. (5) to deduce the corresponding γ values. Taking data from the literature,[22,27,28] we have plotted H *versus* T^2 for mercury, indium, thallium, tin, lead, thorium, and tantalum and find that only in the case of mercury does a straight line accurately fit all of the data. For the other metals, the linearity is

TABLE II. Comparison of γ-values for various metals.

(1) Element	(2) Atomic volume[a] (cm³)	(3) $-(dH_c/dT)_{T_c}$ (oersteds/deg)	γ values (cal/mole deg²) ×10⁴ (4) $\frac{V}{8\pi}\left(\frac{dH_c}{dT}\right)^2_{T_c}$	(5) $\left(\frac{d\Delta S}{dT}\right)_{T=0}$	(6) Calorimetric
Mercury	13.9	199[b] 197[c]	5.2 5.1	3.8[b] 4.5[d]	...
Indium	15.7	144[d]	3.1	3.5[c] 3.6[d]	3.23[f]
Thallium	17.2	137[c] 139[d]	3.1 3.2	2.8[c] 3.4[d]	...
Tin	16.3	150[b]	3.5	3.5[b] 3.95[c]	4.0[g]
Lead	18.3	212[c]	7.8	7.1[b] 7.0[c]	...
Titanium	10.7	285[e]	...	...	8.3[h]
Zirconium	14.1	230[e]	...	...	6.9[h]
Thorium	19.8	191[i]	6.9	...	...
Vanadium	8.39	436 ± 20	15	...	...
Tantalum	10.9	369 ± 10[b]	14	19[b]	14.1[j]
Uranium	12.5	$\gtrsim$530[e]	...	...	$\gtrsim$34[k]

[a] Atomic volumes were calculated from data given in reference 12 from densities at 20°C, except for Hg for which $V_{-195°\text{C}}$ is used.
[b] Reference 22.
[c] Reference 27.
[d] Reference 28.
[e] Estimated from column 6.
[f] J. R. Clement and E. H. Quinnell, Low Temperature Symposium, U. S. Bureau of Standards, March 27–29 (1951).
[g] W. H. Keesom and P. H. van Laer, Physica 5, 193 (1938).
[h] These data were kindly supplied by Dr. S. Friedberg, Carnegie Institute of Technology, in advance of publication.
[i] Reference 3. From reference 26 it may be inferred that both T_c and $(dH_c/dT)_{T_c}$ for thorium are somewhat higher than the values reported by Shoenberg.
[j] W. H. Keesom and M. Désirant, Physica 8, 273 (1941).
[k] Reference 8.

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[23] W. Meissner and H. Westerhoff, Z. Physik **87**, 206 (1934).

[24] C. J. Gorter and H. Casimir, Physica **1**, 306 (1934).

[25] J. A. Kok, Physica **1**, 1103 (1934).

[26] B. B. Goodman and E. Mendoza, Phil. Mag. **42**, 594 (1951).

[27] Daunt, Horseman, and Mendelssohn, Phil. Mag. **27**, 754 (1939).

[28] A. D. Misener, Proc. Roy. Soc. (London) **A174**, 262 (1940).

quite good in the neighborhood of T_c. As T decreases to 0, the H_c, T^2 curve rises progressively above the line representing the data in the vicinity of T_c. Now it can be shown that in order for (5) to be valid it is only necessary for (4) to represent the data in the vicinity of T_c. Hence it is convenient to obtain the slope of the H_c, T^2 curve at T_c, from which we obtain $(dH_c/dT)_{T_c}=2T_c[dH_c/d(T^2)]_{T_c}$. In Table II are compared γ-values obtained in three ways: by direct calorimetric measurements, from Eq. (3), and from Eq. (5). It will be noted that the values of γ derived from Eq. (5) agree with the calorimetric determinations at least as well as do those obtained from Eq. (3). In particular, the excellent agreement in the case of the hard superconductor tantalum lends support to the applicability of the relation to data which follow the parabolic law (4) accurately only in the vicinity of T_c. The evaluation of γ from data in the range near T_c rather than near 0°K has a further advantage arising from the fact that B, H curves are generally most reversible in the vicinity of T_c, particularly for hard superconductors.† A plot of the penetration fields *versus* T^2 for vanadium specimen B gives a curve rather similar to that of tantalum but with somewhat greater scatter of the points; the value of γ deduced from Eq. (5) is 15×10^{-4} cal/mole deg^2. Since the γ values for the fourth transition group metals do not vary greatly, our value of γ for vanadium in relation to that for tantalum may be taken as a confirmation of the assumption that the penetration fields of Fig. 6 are not too far different from the equilibrium fields that would be characteristic of a pure, unstrained specimen of vanadium. By the same token, it seems clear that the very high critical fields reported for niobium,[5] which imply a $\gamma=375\times10^{-4}$ cal/mole deg^2, are far from the equilibrium fields.[29] Goodman and Shoenberg[8] have reached similar conclusions in evaluating their measurements of the high critical fields of uranium.

CONCLUSIONS

The foregoing indicates that the magnetic properties exhibited by most specimens of the so-called hard superconductors are due to internal strain arising from either mechanical work or interstitially located impurities such as carbon, nitrogen, and oxygen. The very large effects of small concentrations of these impurities on the superconductive properties can be understood on this basis. As shown by Shoenberg's work[3] on thorium, whose structure and large atomic volume reduces the strains introduced by these impurities, a sufficiently pure specimen of a metal in the fourth and fifth transition groups will have a reversible B, H curve, and in general will have properties identical with those of the soft superconductors. It is difficult to correlate our results with Webber's studies[7] on the effect of annealing and gas content on the superconducting properties of tantalum; part of the difficulty may result from the fact that resistance measurements do not necessarily reflect the properties of the bulk material.

From an evaluation of γ in terms of $(dH_c/dT)_{T_c}$, it appears that sharp penetration fields, in the case of those specimens that do not exhibit a reversible B, H transition, are not far different from the equilibrium fields. A direct calorimetric study of vanadium is under way to test these views. It is also planned to correlate the superconductive properties of the hard superconductors with internal friction studies[30] which give direct evidence of the concentrations of interstitial impurities.

ACKNOWLEDGMENTS

We wish to thank our many colleagues who contributed to this work either directly or indirectly. Special thanks are due to Dr. Suzanne Beatty for the x-ray studies, to W. J. Houk for the hardness measurements, to R. L. Anderson for the metallographic work, and to J. W. McWhirter for the residual resistance ratio measurements.

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† *Note added in proof.*—The data tabulated in Table II indicate the general validity of (5), which provides a check on the expected magnitude of the equilibrium $(dH_c/dT)_{T_c}$ in terms of the normal electronic specific heat. Since (5) follows from the assumption of (4) as the equilibrium H_c, T relation, then by virtue of (2) the form of $\Delta C=C_s-C_n$ is determined to be a sum of a term linear in T and one cubic in T. Conversely, it has been shown [see G. Preston Burns, Phys. Rev. **76**, 999 (1949)] that if the specific heat of the normal state is given by $C_n=\gamma T+AT^3$ and that of the superconducting state by $C_s=BT^3$, where γ, A, and B are constants, the form of the equilibrium H_c, T relation must be (4).

[29] At the Oxford Conference on Low Temperatures, at which the present paper was read, A. Brown, M. W. Zemansky, and H. A. Boorse reported a calorimetric determination of γ for niobium to be 21.0×10^{-4} cal/mole deg^2, which is in direct support of the conclusion indicated above.

At the same meeting, L. C. Jackson and H. Preston-Thomas reported that niobium, when heated in a high vacuum at 2300°K for 40 hours, exhibited a very appreciable lowering of the initial dH_c/dT as measured both by resistance and magnetic methods. The transition temperature after heat treatment was raised from pre-heat treatment values of 8.35°K for the magnetic method and 8.75°K for the resistance method to a common value of 9.20°K. The mechanical hardness of the metal was observed to decrease greatly as a result of the heat treatment. These results are entirely consistent with the work presented in this paper.

[30] T'ing-Sui Kê, Phys. Rev. **74**, 9 (1948).