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Superconducting Elements

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IN the last twenty years a considerable amount of experimental work has been done on the magnetic and thermal properties of the superconducting elements. The number of elements known to be superconducting in bulk form at zero pressure has been increased to 22, the temperature range of the measurements has been extended down to about 0.1°K, and the effects produced by physical and chemical impurities have been studied. Much additional work will be necessary, however, before complete and reliable data concerning transition temperatures, threshold field curves, and specific heats are available.

One of the important advances in experimental technique during this period has been the use of magnetic methods to detect the transition between the normal and the superconducting states. Previously, the vanishing of the resistance of a specimen had been taken as the criterion for the onset of superconductivity. Detection techniques based on resistance measurements have the disadvantage that the resistance drops to zero as soon as there is a superconducting path through the specimen. The zero resistance along such a path may not be characteristic of the specimen as a whole, and erroneous values for the transition temperature and critical fields may therefore be obtained. The magnetic detection methods are not so sensitive to the existence of inhomogeneities in the specimen. In fact, an estimate of the fraction of a specimen which is superconducting can be obtained by measuring the amount of flux expelled during the transition. Both ballistic and ac induction methods have been used successfully to detect the onset and disappearance of superconductivity. For a very pure specimen both the resistance and the magnetic methods yield the same value for the transition temperature.

There has also been increasing recognition of the necessity for using very pure specimens. The transition temperatures of some of the elements can be changed appreciably by adding small amounts of impurities or by physically straining the specimen, for example by cold work. It has been customary for some years to distinguish between "hard" and "soft" superconductors. The initial slopes of the critical field curves are of the order of 1000 and 100 oersted/deg, respectively, in the two classes. There is now respectable evidence that the distinction is not a real one. The high critical fields of the hard superconductors are often due to small amounts of various gases located interstitially in the metallic lattices. The impurity atoms strain the lattice. Absorbed gas is not considered usually when the impurity content is determined. It would be useful to have data on superconductors with carefully controlled and varied impurity contents. So far, only a few such experiments have been performed.

The transition temperature may also be affected by the coexistence of two lattice structures. Usually only one structure is stable at low temperatures (and effectively zero pressure), but the transition to the stable phase may not take place at an appreciable rate. To avoid this difficulty it is obviously desirable to work with spectroscopically pure specimens, preferably in the form of single crystals, and otherwise vacuum annealed to remove internal strains.

If the superconducting transition is thermodynamically reversible, the electronic specific heat can be calculated from the threshold field data. The values of the specific heats so obtained are frequently in good agreement with the calorimetric determinations. However, in some cases, discrepancies up to an order of magnitude exist. These discrepancies have been attributed to the circumstance that the magnetic and the calorimetric measurements were made in different temperature regions, but the evidence is not conclusive. In any case it seems desirable to have magnetic and thermal data on the *same* specimen. To the writer's knowledge such experiments have not yet been done.

At temperatures below 1°K it is very difficult to make reliable measurements. The metallic specimen

must be cooled by contact with a paramagnetic salt. However, the low values of thermal conductivities in this region make it hard to insure that there is good thermal contact. The usual practice has been to use a finely divided specimen mixed with the powdered salt, but no high accuracy will ever be obtained with this procedure. Measurements of the magnetic field and temperature are serious problems. Because of demagnetization effects the field which acts on the specimen is not the external applied field. Temperature measurements are necessarily somewhat uncertain because they are based on magnetic scales whose relationships to the absolute thermodynamic scale have not yet been definitely established.

The calorimetric measurements which seem desirable would be subject, below 1°K, to the additional difficulty that the heat capacities are extremely small. However, sooner or later experimental techniques will probably be developed to the point where the measurements are feasible.

In the following sections most of the experimental work on the threshold field curves and specific heats of pure superconducting elements which has been done since about 1935 is reviewed. There are a few references to earlier work if the data are still of interest. As a rule the experimental techniques used in the 1°–4° range will not be discussed. If there are more comments, some of them critical, on one paper rather than another, one should not infer that the experimental work was poorer. It is more likely that the authors gave more detail, or else that the paper is of greater interest. One should also not infer that the experimentalists were unaware of the difficulties and sources of error.

The following notations will be used:

T_c: transition temperature in zero external field
H_0: critical field at absolute zero
γ: coefficient of the term linear in T in the specific heat
Θ: Debye characteristic temperature.

In accordance with general practice, the initial slope of the threshold or critical field curve is written as a positive quantity. In actuality, however, it is negative. Also, as is customary, specific heats are given in cal/mole deg although there is little reason for the retention of the calorie as a unit in a region 270° below the freezing temperature of water. If no statement is made concerning the annealing of a specimen, it is probably safe to assume it was not annealed.

The values of T_c obtained in the various experiments have not been corrected to the 1949 scale of temperature for two reasons: (1) The correction is usually smaller than the uncertainty in the measurements, and (2) a further correction would have to be applied when the 1949 scale is superseded.

ALUMINUM

A calorimetric determination of the specific heat of Al was made by Kok and Keesom (K8).* The specimen used was 99.7 percent pure. The transition temperature was observed to be 1.13°K, and the initial slope of the critical field curve as determined from the discontinuity in the specific heat was 143 oersted/deg. The Debye characteristic temperature was found to be 419°K, and the electronic specific heat was found to be $3.484\times10^{-4}T$ cal/mole deg. These values must be accepted with some caution: (1) All temperatures were based on the 1932 scale. To correct the specific heat data to the 1949 scale would require extensive calculations, since the computed heat capacities as well as the temperatures are affected by the change of scale. These calculations are probably not worth while since Kok and Keesom state that the temperatures given in the paper may be a little low. (2) The comparative impurity of the specimen and the failure to anneal and outgas it may account for the discrepancy between these T_c and $(dH/dT)_{T=T_c}$ values and those given below. In any case, a direct measurement of the critical field is likely to be more accurate than a value computed from thermal data.

Shoenberg (S7) used a ballistic induction method to determine the transition temperature of several specimens which were 99.99 percent pure and one which was 99.995 percent pure. He found that T_c was 1.150°K (on the 1932 scale) and dH/dT had an initial value of 140 oersted/deg. As he has pointed out, these results are probably somewhat in error because in determining the temperature no allowance was made for the pressure drop between the liquid helium and the top of the dewar flask. The measurements were made between 0.98° and T_c.

Daunt and Heer (D3) measured the critical fields at temperatures between 0.45 and 0.74°K. They used 30 mesh aluminum chips (of the order of 1 mm in linear dimensions), the purity being greater than 99.9 percent. These chips were imbedded in powdered potassium chrome alum, and the mixture was compressed (200–300 atmospheres) to form an ellipsoidal pill. This method was adopted in an attempt to insure thermal equilibrium between the superconducting sample and the paramagnetic salt used for cooling. The chips were irregular in shape and, moreover, the method of preparation of the sample undoubtedly produced internal strains in the metal particles. Consequently, the transition was not very sharp, and there was also some uncertainty concerning the actual field which acted on the aluminum. According to Daunt and Heer this uncertainty was only about 1 percent in the temperature region covered in the experiments. The Curie temperature, in terms of which the results are given, is said to be the same, within the accuracy of the experiments, as the absolute temperature. In general, in experiments where a compressed powder

* References in ( ) are given at the end of the paper.

is used as a thermometer, it is desirable to calibrate it against some better known standard because of the possibility that the compression may alter the thermodynamic properties of the salt.

Daunt and Heer report that the critical field curve is not exactly parabolic. Because of the necessity for extrapolation over a wide range, no reliable values of H_0 or T_c can be obtained from their data. The calculated value of the electronic specific heat is $2.59\times10^{-4}T$ cal/mole deg.

In Goodman's (G1) letter in *Nature*, only the values 1.197°K for T_c and 106 oersted for H_0 are given.

The experiments of Goodman and Mendoza (G2) were on a machined ellipsoid with axial ratio 4:1. The specimen was 99.995 percent pure and was annealed in a helium atmosphere to remove internal strains. It was cooled by contact through a copper rod with a paramagnetic salt. The transition was determined by measuring the effective ac susceptibility of the specimen in a low-frequency field. This quantity depends on the currents flowing in the specimen, and therefore the method measures the resistance rather than the magnetization. A correction was applied to take account of the fact that because of the non-zero demagnetizing coefficient the substance enters the intermediate state at a value of the field lower than the true critical field.

Goodman and Mendoza's measurements extended from the zero field transition temperature down to 0.1°; the threshold field curve is stated to be accurately parabolic with T_c equal to 1.197°K (1949 scale) and H_0 equal to 106.0 oersted. The value of the electronic specific heat deduced from the threshold field curve is $2.95\times10^{-4}T$ cal/mole deg. The temperatures were measured on a magnetic scale, and corrected to the absolute scale, by using published data on the magnetic and thermal properties of the paramagnetic salts. Goodman and Mendoza obtained the same transition temperatures to within 0.01° for a zinc specimen with iron ammonium alum and potassium chrome alum as thermometers although T^* and T differed by amounts up to 0.03° for these two salts. It should be noted that the relation between the magnetic scale and the absolute scale of temperature cannot be regarded as definitely established for either iron ammonium alum or potassium chrome alum. Existing comparisons of the scales are based on assumptions about the local field corrections and on erroneous values of the crystalline field splitting of the low-lying energy levels of the paramagnetic ions. Moreover, these splittings are possibly altered by applying pressures of the order of 2000 atmospheres as was done by Goodman and Mendoza.

TITANIUM

The early attempts to determine the transition temperature of titanium involved measuring a change of resistance; this method is particularly unreliable in the case of a "hard" superconductor. For example, de Haas and van Alphen reported a T_c of 1.63°K for an impure specimen. Later workers used a magnetic method to detect the transition. Shoenberg (S7) found that the transition temperature was not above 1°K for a specimen 99.9 percent pure. He suggested that the superconductivity reported earlier was due to the presence of superconducting TiC or TiN. The suggestion that titanium alloys might be responsible for the transition observed was also made by Webber and Reynolds (W2) following their resistance measurements on a wire approximately 99.7 percent pure.

Daunt and Heer (D2) used a specimen of 99.95 percent purity distributed in the form of particles 2–3 mm in linear dimensions through powdered potassium chrome alum. The mixture of salt and metal was formed into an ellipsoidal pill of axial ratio 2:1 by applying pressures of 200–300 atmospheres. A ballistic mutual inductance method was used to detect the transition which, in zero magnetic field, was found to occur at 0.527°K. The threshold field curve was determined down to 0.3° and was found to have an initial slope of 470 oersted/deg. This high value of dH_c/dT puts Ti in the group of "hard" superconductors. Daunt and Heer therefore made no attempt to derive the value of the electronic specific heat from their threshold field measurements. The same remarks concerning the preparation of the specimen and the measurements of critical fields and temperatures which were made about the experiments of Daunt and Heer on Al apply also to their experiments on Ti.

Estermann, Friedberg, and Goldman (E1) determined the specific heat between 1.8 and 4.2° by a calorimetric method. The Debye characteristic temperature was found to be 280°K, and the electronic specific heat was found to be $8.00\times10^{-4}T$ cal/mole deg. The purity of the specimen they used exceeded 99 percent.

Smith and Daunt (S10) used the same specimen as Daunt and Heer but annealed it for 2.5 hours at 800°C. The transition temperature and initial slope of the critical field curve were 0.558°K and 450 oersted/deg, respectively, after annealing. Even after heat treatment the superconducting transition was not reversible, and therefore the electronic specific heat was not calculated.

Smith, Gager, and Daunt (S11) used a specimen whose purity was 99.99 percent. It was vacuum annealed for 3 hours at 670°C. T_c was found to be only 0.387° on a magnetic scale and $(dH_c/dT)_{T=T_c}$ was 89.5 oersted/deg. This latter value is small enough to enable one to classify Ti with the "soft" superconductors. Extrapolation of the measurements, which were made between 0.272 and 0.387°, indicated that the critical field at absolute zero was about 20 oersted. The threshold field curve was approximately parabolic. The electronic specific heat deduced therefrom was $1.1\times10^{-4}T$ cal/mole deg, which is smaller by an order of magnitude than the calorimetrically determined value.

Steele and Hein (S13) have reported measurements

on two Ti specimens; one specimen was a cold worked wire with a purity of 99.98 percent, and the other an unannealed crystal bar with a purity exceeding 99.99 percent. The wire was divided into small pieces and pressed into a pill with potassium chrome alum, so that the necessary low temperatures could be reached by adiabatic demagnetization. The Ti crystal was attached to a potassium chrome alum pill by means of a copper rod. For the wire, the zero field transition temperature was found to be 0.37°K, the initial slope of the critical field curve being 465 oersted/deg. For the crystal bar T_c was 0.49°K, and the initial slope was 400 oersted/deg.

The wide discrepancies between different observers and, indeed, between different specimens studied by the same experimentalists must be attributed either to experimental error or inherent differences in the specimens. Steele and Hein are of the opinion that their titanium bar was not very different from the specimen used by Smith, Gager, and Daunt. Nevertheless, in view of similar discordant results obtained on other hard superconductors, it appears reasonable to attribute part of the discrepancy to dissimilarity of the specimens used. The errors involved in the temperature measurement are certainly small in comparison with the scatter of the T_c values. However, as Steele and Hein point out, it is difficult to insure thermal equilibrium between the metal and the salt; part of the discrepancies may be attributable to failure to establish thermal equilibrium.

VANADIUM

Wexler and Corak (W4) have obtained strong evidence that the anomalous properties of the hard superconductors are due to small quantities of gases in interstitial positions in the lattices. The gases set up internal strains which cannot easily be removed by vacuum annealing as can the strains arising from mechanical working.

A ballistic mutual inductance method was used by Wexler and Corak to detect the transitions. Their measurements were made on five specimens which contained less than 0.1 percent Fe and of the order of 0.1 percent of other metals. These relatively high metallic impurity contents probably have an appreciable influence on the observed transition temperatures and magnetization curves. More interesting, however, is the fact that the specimens also contained from 0.038 to 0.15 percent oxygen and 0.021 to 0.189 percent nitrogen. The experiments showed that the greater the gaseous impurity content the greater the departure of the specimen from ideal superconducting behavior. For the purest specimen the transition temperature was 5.13°K, and the initial slope of the critical field curve was 436±20 oersted/deg. The value of γ, the coefficient in the electronic specific heat term, computed from measurements of the critical field near the zero field transition temperature, is 15.0×10^{-4} cal/mole deg^2.

The specimens used by Webber, Reynolds, and McGuire (W3) were spheres approximately $\frac{1}{8}$ inch in diameter, 99.7 and 99.8 percent pure. The transitions were detected by using an ac mutual inductance method. The initial slopes of the transition curves were 5000 and 4100 oersted/deg. In zero field the transition extended over a temperature range of about 1°. One can conclude on the basis of Wexler and Corak's work that these specimens probably contained a good deal of gas in interstitial positions in the lattice.

Boorse, Zemansky, and Worley (unpublished) have made calorimetric measurements on two V specimens. The impurity analyses are as follows:

	% Impurities by weight				
Sample	N	O	U	C	Fe
V–I	0.132	0.13	0.0055	0.045	···
V–II	0.04	0.08	0.008	0.054	···

The specific heat measurements yielded the following results:

Sample	T_c (°K)	Width of transition	γ (cal/mole deg^2)	Θ (°K)
V–I	4.69	4.66–4.85	21.9×10^{-4}	321
V–II	4.99	4.93–5.05	21.4	274
V–IIA	4.89	4.82–4.96	21.1	273

Sample IIA was produced by annealing Sample II for one hour at 1800°C and a pressure of 10^{-4} mm Hg.

ZINC

A calorimetric determination of the specific heat was made by Keesom and van den Ende (K3). They found a Debye characteristic temperature of 320°K. According to Silvidi and Daunt's (S9) interpretation of their measurements the value of γ is 1.25×10^{-4} cal/mole deg^2.

Keesom (K1) measured the resistance of a cold worked specimen of unstated purity. He found that T_c was 0.79°K (1932 scale).

Shoenberg (S7) used a specimen whose purity was 99.999 percent. The metal was embedded in a ferric alum pill which was cooled by the adiabatic demagnetization procedure. The transition temperature was determined on a magnetic scale by observing the magnetic moment of salt and metal together as they warmed up. Shoenberg found the transition temperature was 0.84 ±0.05°K. This value is somewhat uncertain since short warm-up times indicated that the salt and the zinc may not have been in thermal equilibrium. The initial slope of the critical field curve was found to be about 100 oersteds/deg.

The procedures used by Daunt and Heer (D3) in their work on Zn were the same as they used for Al and subject to the same uncertainties. The Zn specimens were 99.999 percent pure. In one the particle size was of the order of 1–2 mm and in the other 0.1–0.5 mm. No significant difference in the critical field curve was noted and, indeed, none was to be expected since the smallest particle size far exceeded the penetration depth of the magnetic field. The surface contributions to the

specific heat were also probably inappreciable. The measurements extended from a Curie temperature of 0.283° to the zero-field transition temperature which was found to be 0.959° and 0.910° in the two specimens. The critical field curve was not exactly parabolic. Its initial slope was 98 oersted/deg, which agrees well with Shoenberg's value. The electronic specific heat was calculated to be $1.36\times10^{-4}T$ cal/mole deg and the specific heat in the superconducting state to be $4.8\times10^{-4}T^3$ cal/mole deg.

Silvidi and Daunt (S9) made a calorimetric determination of the specific heat of two Zn specimens in the normal state. One was a powder with an average particle size of 1.3×10^{-4} cm, and the other was a solid made by fusing the powder. The purity of the material was 99.9 percent. In the temperature range from 1.5 to 3.5°K the specific heat of both specimens could be represented by $[464.5\ (T/291)^3+1.50\times10^{-4}T]$ cal/mole deg.

The values of T_c and H_0 given by Goodman (G1) are 0.905°K and 53 oersted, respectively.

The measuring technique of Goodman and Mendoza (G2) is discussed above under Al. The Zn specimen used was an ellipsoid of length 27.5 mm and diameter 6.8 mm. Its purity was 99.999 percent, and it was annealed in a helium atmosphere to remove internal strains. The measurements extended to 0.1°. According to Goodman and Mendoza, the usual parabolic relationship between critical field and transition temperature held very well. They found that T_c was 0.905°K, H_0 was 52.5 oersted, and γ was 1.16×10^{-4} cal/mole deg^2. There is, of course, some uncertainty concerning the absolute temperature due to the use of potassium chrome alum and iron ammonium alum as thermometers and some uncertainty concerning the critical field because of the nonzero demagnetizing factor.

GALLIUM

Shoenberg (S7) used a specimen which was 99.94 percent pure. It was in the form of a thin rod cast in a glass tube. In the case of gallium, annealing occurs at room temperature. A ballistic induction method was used to determine the critical fields. The transition temperature found by Shoenberg was 1.056 ± 0.010°K (1932 scale), and dH_c/dT had the initial value 88 ± 5 oersted/deg. For the reason previously given, T_c may be somewhat in error.

According to Goodman (G1), T_c is 1.103°K and H_0 is 51 oersted. Goodman and Mendoza (G2) give the same value for T_c and state that H_0 is 50.3 oersted. They used a specimen whose purity was about 99.99 percent. The measurements, which extended to 0.1°, are discussed above under Al. The threshold field curve was nearly parabolic. The electronic specific heat was calculated to be $0.91\times10^{-4}T$ cal/mole deg.

Gallium has a highly anisotropic electrical resistivity. Conceivably, the transition temperature of a gallium single crystal in a magnetic field could depend on the direction of the field relative to the crystal axes. Croft, Olsen-Baer, and Powell (C7) made resistance measurements on several single-crystal specimens of high purity. They found that the transition temperature varied with the direction of the field by less than 0.002°.

ZIRCONIUM

The superconductivity of Zr was discovered by Kurti and Simon (K9). Their experiments, in which superconductors were cooled by contact with adiabatically demagnetized paramagnetic salts, were the first of this type. They used a mixed specimen consisting of small pieces of Zr, 1–2 mm in size, dispersed through an equal volume of iron ammonium alum, the whole being compressed into a pill. Kurti and Simon state that the Zr was prepared by crystallization from the gaseous phase and was of high purity. A ballistic mutual inductance method was used for the determination of the superconducting transition and for the measurement of the temperature. The measurements, which were made between 0.4° and 0.7°K, yielded a transition temperature of 0.70° and an initial slope of the critical field curve of approximately 400 oersteds/deg. Kurti and Simon pointed out that the necessity for making local field corrections and the irregularity of the shapes of the particles adversely affected the accuracy of the experiments. Since Zr is a hard superconductor, traces of oxygen or nitrogen in interstitial positions in the lattice may also have affected the behavior.

A calorimetric determination of the specific heat was made by Estermann, Friedberg, and Goldman (E1). Their measurements, which were made on a specimen of 99.5 percent purity, extended from 1.8° to 4.2°K. The Debye characteristic temperature was found to be 265°K and the electronic specific heat to be $6.92\times10^{-4}T$ cal/mole deg.

Smith and Daunt (S10) determined the threshold field curve by a magnetic method for a specimen of 99.9 percent purity. The principal impurity was 0.04 percent hafnium. The specimen was in the form of a bar $11\times5.5\times3.3$ mm. When it was tested as supplied the transition temperature was 0.565°K and the initial slope of the threshold field curve was 335 oersteds/deg. After annealing for $2\frac{1}{2}$ hours at 800°C, these values dropped to 0.546°K and 170 oersteds/deg. The threshold field curve for the annealed specimen was approximately parabolic, the value of H_0, extrapolated from the measurements between 0.314 and 0.546°, being 46.6 oersted. The calculated value of γ was 3.92×10^{-4} cal/mole deg^2. The large discrepancy between the calculated value of γ and the value obtained from specific heat measurements was tentatively ascribed by Smith and Daunt to metastable inclusions of body centered cubic structure in specimens which had not been carefully annealed. This hypothesis can be checked, and it would be very interesting to have it done.

NIOBIUM

Niobium is a particularly interesting superconductor because of the high value of the transition temperature (over 8°K) and the high values which have been reported for the initial slope of the critical field curve.

The measurements of Daunt and Mendelssohn (D5) extended only from 1.5° to 4.2°K, and therefore very few conclusions could be drawn from them. Moreover, the purity of their specimen was only about 99.8 percent. In zero field there was approximately 20 percent frozen-in flux (absence of complete Meissner effect) which is characteristic of alloy behavior. In the later paper of Daunt, Horseman, and Mendelssohn (D4) the value of T_c is given as 8.4°K, and H_0 is stated to be 2590 oersteds.

The difficulties involved in obtaining a pure specimen of Nb have been discussed by Cook, Zemansky, and Boorse (C6). Not only is it very difficult to separate Ta from Nb, but it is also difficult to determine the residual amount of Ta. In the specimens used by Cook, Zemansky, and Boorse the Ta content was believed to be of the order of 0.2 percent with other impurities in total amount up to 0.1 percent present. A series of vacuum annealed specimens was used. It is not certain, however, in view of the work of Wexler and Corak (W4) on V, that vacuum annealing will make a Nb specimen more closely approximate the behavior of an ideal superconductor. An ac susceptibility method was used for detecting the transitions. The measurements were made between 5.0° and 9.0°K in fields up to 6000 oersted. The zero-field transition was spread over about 0.15°. The critical field curve obtained was very nearly parabolic with T_c equal to 8.65°K and H_0 equal to 8250 oersteds. The initial slope of the critical field curve was 1910 oersted/deg. It seems likely that this value is much higher than that which would be characteristic of a very pure specimen. It is somewhat risky to calculate γ from the threshold field curve, but the value so obtained is 375×10^{-4} cal/mole deg^2. The calculated Debye temperature in the superconducting state is 67°K.

The results of Jackson and Preston-Thomas (J1) also indicate the difficulty of working with Nb. They detected the transition by resistance, ballistic, and ac inductance measurements. The data on the critical field curve obtained by the three methods differed appreciably, as did the results on two different specimens. The data were not inconsistent with those of Cook, Zemansky, and Boorse, however, the transition temperatures for the two specimens being 8.85° and 8.35°K and the initial slopes of the threshold field curves being 1050 and 1900 oersted/deg.

Specific heat measurements by the calorimetric method were made between 2.5° and 20°K by Brown, Zemansky, and Boorse (B1). In the superconducting state they found c_s was 464 $(T/161)^3$ cal/mole deg, although at the lower temperatures the experimental points fell somewhat below this curve. Between 7.5° and 12°K the specific heat could be represented by the formula

$$c_n=[21\times10^{-4}T+464(T/254)^3] \text{ cal/mole deg.}$$

At 20°K the Debye characteristic temperature was 268°K. If one assumes that the threshold field curve is parabolic and applies the usual thermodynamic relations one deduces values 8.7°K for T_c and 1960 oersted for H_0. This value of H is much lower than the one deduced from the magnetic measurements, a result to be expected since impurities will not affect the specific heat measurements as much as they will the direct critical field determinations.

Further calorimetric measurements were made by Brown, Zemansky, and Boorse (B2) on an annealed, strain-free specimen whose purity was estimated as 99.8 percent. Data were taken in the range 2.5° to 11°K in zero field and in a field of 5000 oersted. In the normal state the experimental points could be fitted to the usual curve $\gamma T+464T^3/\Theta^3$ with $\gamma=20.4\times10^{-4}$ cal/mole deg^2 and $\Theta=252$°K. The transition to the superconducting state occurred at 8.70±0.10°K. The threshold field curve derived from the specific heat data was found to be nearly parabolic, the value of H_0 being 2000 oersted and the initial slope of the curve being 453 oersted/deg.

TECHNETIUM

Daunt and Cobble (D1) used a powder specimen prepared from fission waste products. The mass available was 0.103 g and the purity of the metal exceeded 99.9 percent. The transition took place over a range of a few degrees; the value quoted by Daunt and Cobble for T_c is 11.2°K. Largely because of the geometrical form of the specimen, the transitions in a magnetic field were irreversible. The value of $(dH/dT)_{T=T_c}$ lies between 300 and 400 oersted/deg.

RUTHENIUM

The superconductivity of ruthenium was discovered by Goodman (G1). He detected the transition by observing the change in susceptibility of the specimen in an ac field. No details concerning the purity or preparation of the specimen are given in his brief paper. The critical field curve is said to be parabolic with T_c equal to 0.47°K and H_0 equal to 46 oersted.

The superconductivity of Ru and Os is of interest because these elements are the only known superconductors among the elements in Group VIII of the periodic table.

CADMIUM

Although Tuyn (T1) reported that Cd is a superconductor, his observations were probably on an alloy in view of the high transition temperature (2.62°K)

he gives and the fact that another specimen he tested was not superconducting down to 1.46°.

The discovery of the superconductivity of Cd should, perhaps, be credited to Kurti and Simon (K9). The method used by them has been discussed in the section on Zr. The purity of their Cd sample is not stated in their paper. They used three different specimens—fine filings, grains 1–2 mm in size, and small rings. The Cd was mixed with manganese ammonium sulfate and pressed into a pill. The zero-field transition was found to occur at a magnetic temperature of 0.54 $\pm 0.02°$ and the initial slope of the critical field curve to be about 100 oersted/deg.

Goodman (G1) obtained the values 0.560°K for T_c and 29 oersted for H_0. According to Goodman the critical field curve is accurately parabolic. Therefore the intial slope of the curve is 103 oersted/deg, in good agreement with the value obtained by Kurti and Simon.

The measurements of Goodman and Mendoza (G2) were made on an ellipsoidal specimen, 28.5 mm long and 7.1 mm in diameter. It was 99.996 percent pure and was annealed. The experimental technique is discussed above under Al. The measurements extended to 0.1°K. The results are that T_c is 0.560°K, H_0 is 28.8 oersted, and the value of γ derived from the threshold fields is 1.28×10^{-4} cal/mole deg^2.

An ac inductance method was used by Samoilov (S1a) to detect the transition. He found the critical field curve to be parabolic with T_c equal to 0.547 ± 0.005°K and H_0 equal to 28.4 ± 0.3 oersted.

The experiments of Steele and Hein (S12) were on small spheres of spectroscopically pure Cd prepared by stirring the molten metal with a high boiling point silicone oil. In one specimen the spheres were 2.2–3.1 $\times10^{-3}$ cm in radius, and in another they were 6–12 $\times10^{-2}$ cm in radius. These spheres were mixed with potassium chrome alum and compressed into cylinders 1.75 cm in diameter and 2.2 cm long. It is rather difficult to say what the demagnetization correction should be for such fat cylinders. The zero-field transition temperature was found to be 0.65°K. The initial slope of the critical field curve was found to increase with decreasing size of the Cd spheres. From the experimental curves of Steele and Hein one can infer that, at least for the smaller spheres, H_0 is appreciably higher than the value given by Goodman and Mendoza. It is difficult to reconcile the markedly different values of T_c found by these two pairs of experimenters. Even the smallest spheres used by Steele and Hein were probably large in comparison with the penetration depth of the magnetic field. Moreover Cd is a soft superconductor so one would not expect physical strains or small amounts of impurities to influence the behavior to any great extent. Consequently, the observed differences between the small and the large spheres are also hard to understand. Clustering of the spheres may have affected the observed behavior.

Smith and Daunt (S10) used a specimen of 99.99 percent purity which was annealed at 150°C for $1\frac{1}{2}$ hours. It was in the form of an ellipsoid whose axes were 19 and 6 mm. Measurements were made between 0.369 and 0.60°K. The data can be fitted by assuming the threshold field curve is parabolic with T_c equal to 0.602°K and H_0 equal to 33.8 oersted. The initial value of dH/dT was found to be 112 oersted/deg. The value of the electronic specific heat calculated from the magnetic data is $1.54\times10^{-4}T$ cal/mole deg.

It is clear that the results of different observers in the region below 1°K are far from agreeing.

The only available low-temperature calorimetric data were obtained by Samoilov (S1b). These data are not entirely consistent with the magnetic data if the threshold field curve is assumed to be parabolic. Clement (C1) has discussed Samoilov's results and has shown that the thermal and the magnetic data can be reconciled if one assumes that the threshold field curve is cubic rather than parabolic. According to Clement, the best value of γ is 1.70×10^{-4} cal/mole deg^2, Θ is 300°K, and H_0 is 29.7 oersted. The value of T_c is 0.555°K and $(dH_c/dT)_{T=T_c}$ is 53.5 oersted/degree.

INDIUM

Daunt, Horseman, and Mendelssohn (D4) used a specimen of 99.98 percent purity which was cast *in vacuo* into nearly spherical form. A magnetic method was used to determine the transition temperatures for various values of the applied external field. Measurements were made between 1° and T_c which was found to be 3.40°K (1932 scale). The experimental points fall along a parabola characterized by T_c and a value 275 oersted for H_0. The electronic specific heat was calculated to be $3.5\times10^{-4}T$ cal/mole deg.

Misener (M6) used a specimen whose purity was 99.985 percent which was cast into a long wire. A ballistic mutual inductance method was used to detect the transitions. Threshold field determinations were made between 1.1° and T_c and a least squares method then used to fit a polynomial to the critical field curve. The result is expressed by the formula

$$H_c=269.18-14.86T^2-6.840T^3+1.299T^4-0.015T^5.$$

T_c was found to be 3.368°K (1937 scale) and the value of γ was computed to be 3.6×10^{-4} cal/mole deg^2. The specific heat in the superconducting state was found to vary with temperature as T^4. This result must be regarded with some skepticism. Although there is no theoretical reason why the specific heat in the superconducting state should vary as T^3, it is nevertheless true that a T^3-law seems to be appropriate for many superconductors.

Stout and Guttman (S14) made induction measurements on a single-crystal specimen of approximately 99.95 percent purity. Their data could be fitted to a parabolic threshold field curve, the maximum deviation being 1.8 oersted. From their data they inferred that

T_c is 3.374°K, H_0 is 284.3 oersted, and γ is 4.3×10^{-4} cal/mole deg^2.

Clement and Quinnell (C2) made a calorimetric determination of the specific heat. Their data for the superconducting state extend from 2.3° to 3.368°K while the data for the normal state cover the region from 1.7° to 4.3°K. The value of the electronic specific heat obtained from their measurements is $4.0\times10^{-4}T$ cal/mole deg which is in fairly good agreement with the value obtained from the threshold field curves. According to Clement and Quinnell, the specific heat in the superconducting state is more nearly proportional to T^3 than to T^4.

In work reported in a subsequent paper Clement and Quinnell (C4) extended the temperature range of their calorimetric measurements. Data were taken in the superconducting state between 1.8° and T_c, which was found to have the value 3.396°K. The specific heat in the normal state was determined between 1.7 and 21.3°K. A rather detailed statistical analysis of the data yielded the results $\gamma=4.33\times10^{-4}$ cal/mole deg^2, $H_0=278.4$ oersted, and $(dH_c/dT)_{T=T_c}=528$ oersted/deg. One point which is discussed by Clement and Quinnell is that the threshold field data can be fitted about equally well to a quadratic or to a cubic equation in T. If the calorimetric data are also considered, however, it seems necessary to use a threshold field curve which is cubic in T. If the curve is assumed to be parabolic the best value of γ is about 3.90×10^{-4} cal/mole deg^2. It is, of course, not surprising that better agreement between data and empirical curves can be achieved by use of an additional parameter. The interesting fact is that the best values of γ deduced from the two threshold field curves differ by 10 percent. Perhaps the discrepancies between the magnetic and the calorimetric values of γ for other superconductors can be explained in the same way.

The value of Θ determined by Clement and Quinnell varied from 109° at 1°K down to about 101° at 7.5°K and then rose again to a value of approximately 118° at 21°K.

Calorimetric measurements in the range 12°–273°K were made by Clusius and Schachinger (C5). They subtracted from their measured specific heat an amount $3.55\times10^{-4}T$ cal/mole deg to allow for the electronic specific heat. The remainder was approximately proportional to T^3 with Θ between 125° and 140°K.

TIN

Tin is probably the most convenient of all superconducting elements to work with. It is readily available and specimens of very high purity can be prepared. If necessary they can be grown as single crystals. The transition temperature is just a half-degree below the liquefaction temperature of helium. Moreover, the isotopes of tin vary in atomic weight by about 8 percent. Tin is of additional interest because one crystalline modification, usually called white tin, is superconducting while another, called gray tin, is believed not to be. Probably the most precise measurements of superconducting transition temperatures and threshold fields have been made on tin specimens.

De Haas and Engelkes (H1) measured the critical fields of three different single-crystal wires by a resistance method and determined the threshold field curve for a tin sphere by making induction measurements on its equator. They found that T_c was 3.702°K (temperature scale not specified, probably 1932). The value of the critical field at 0°K obtained by extrapolating their data is about 299 oersted.

Keesom and van Laer (K6 and K7) measured the specific heat calorimetrically and also the latent heat of transition at various temperatures. The specimen they used was ellipsoidal with a 5:1 axial ratio and was made from tin of 99.992 percent purity. The observed latent heats and those calculated from the threshold fields agreed to within a few percent. The measured specific heat in the normal state could be fitted between 1 and 3.2°K by the curve

$$c_n=[464.5(T/185)^3+0.00040T]\ \text{cal/mole deg.}$$

Above 3.2° the experimental points lay above this curve. The specific heat in the superconducting state was found to follow a T^3-law with a Debye temperature of about 140°K.

Daunt and Mendelssohn (D5) used a specimen of 99.996 percent purity which was cast *in vacuo* into a sphere. A ballistic mutual inductance method was used for the measurements which were made between 1.5° and T_c. T_c was found to be about 3.70°K. Calculated values of the entropy difference between normal and superconducting states are given in the paper.

Daunt, Horseman, and Mendelssohn (D4) extended the measurements to 1.06°K. From all the data the following values were obtained: $H_0=310$ oersted, $T_c=3.7$°K, and $\gamma=3.95\times10^{-4}$ cal/mole deg^2.

Webber, Reynolds, and McGuire (W3) used a spheroidal single crystal of 99.992 percent purity. An ac inductance method was used to locate the transitions. The midpoint of the zero-field transition curve occured at 3.71°K. Otherwise the critical field curve was identical with that of de Haas and Engelkes.

Recent work on the superconductive properties of tin has involved use of separated isotopes. The first such experiments were performed by Maxwell (M2) who used a specimen containing 83.4 percent Sn^{124} with an average isotopic mass of 123.1 (less than 0.01 percent chemical impurity content) and natural tin with average isotopic mass 118.7. A magnetic method was used to detect the transitions which were found to occur at 3.715°K for the natural tin and 3.662°K for the enriched isotope.

Lock, Pippard, and Shoenberg (A2) made measurements on separated isotopes; the specimens were cast in silica tubes into long wires. Superconductivity was detected by a ballistic method. The specimens were

probably very pure, although no figures are given, and sharp transitions were obtained. The temperatures (1949 scale) at which the ratio of magnetic moment to field strength had half its superconducting value are listed below:

Average isotopic mass	116.2	120.0	123.6
T_c (°K)	3.763	3.707	3.654°

The relationship $T_cM^{\frac{1}{2}}=$const is approximately satisfied by these data. Furthermore, the threshold field curves were found to be geometrically similar, i.e., H/H_0 was the same function of T/T_c for all isotopes. For all three isotopes $(dH_c/dT)_{T=T_c}$ was 142 oersted/deg, and the extrapolated value of H_0/T_c was 81.5 oersted/deg.

Bär, Mendelssohn, and Olsen (A3) made resistance measurements on thin rolled specimens of the same isotopic samples as Lock *et al.* used. The specimens were annealed to remove internal strains. The results, which are given in Table I, differ somewhat from those quoted above, particularly in regard to the critical field curve. The values of H_0 are, of course, extrapolated. Above 3° the transition curves were not parabolic. Below 3° they were similar parabolas.

In a subsequent, more extensive investigation Lock, Pippard, and Shoenberg (L1) again used specimens of a high but undetermined chemical purity which were cast in silica tubes. A ballistic method was used to detect the transitions. The temperatures were determined from the vapor pressure of helium, the 1949 scale being used. T_c was taken to be the temperature at which, in a weak field, the ratio of the magnetic moment of the specimen to the magnetic field had half the value corresponding to complete superconductivity. The principal results are as follows:

TABLE I. Experimental results of Bär, Mendelssohn, and Olsen on separated isotopes of Sn.

M	T_c (°K)	H_0 (oersted)	H_0/T_c (oer/deg)	$(dH_c/dT)_{T=T_c}$ (oer/deg)
116.2	3.764	308	81.8	152
118.7	3.727	305	81.9	163
120.0	3.710	299	80.5	157
123.6	3.653	291	79.9	154

M	T_c (°K)	H_0 (oersted)
116.2 ±0.05	3.767	307.5
119.9 ±0.05	3.712	...
123.75±0.11	3.659	298.6

The relation $T_cM^n=$const with $n=0.462\pm0.014$ is satisfied by the experimental points. The authors consider it unlikely that n should be as high as 0.500. For isotope 116 the critical field curve has the analytical form $H_c=307.5\ (1-1.0720t^2-0.0944t^4+0.3325t^6-0.1660t^8)$ with $t=T/3.767$. This curve also fits the data for isotope 124 and the data of de Haas and Engelkes (when corrected to the 1949 scale) fairly well (to within 1 oersted) when the appropriate values of T_c are inserted. The calculated value of dH_c/dT at T_c is 152 oersted/deg and the experimental value is 151±2 oersted/deg. The calculated electronic specific heat is nearly, if not entirely, independent of isotopic mass. The ratios $\Delta H_0/H_0^{116}$ and $\Delta T_c/T_c^{116}(\Delta H_0=H_0^{124}-H_0^{116})$ were $(2.894\pm0.016)\times10^{-2}$ and $(2.867\pm0.027)\times10^{-2}$, respectively. One infers that the zero-field transition temperatures depend on isotopic mass in the same way as the critical fields at 0°K.

TABLE II. Experimental results of Serin, Reynolds, and Lohman on separated isotopes of Sn.

M	% Sn	T_c (°K)	H_0 (oersted)	H_0/T_c	$(dH_c/dT)_{T=T_c}$
113.6	99.50	3.805	312	82.0	145
118.7	99.995	3.752	304	81.5	144
123.8	99.76	3.659	298	81.4	144

Separated isotopes of Sn have also been studied by Serin, Reynolds, and Lohman (S2). An ac inductance method was used to detect the transitions. The specimens were cast *in vacuo* into long wires. The essential data are given in Table II. Measurements were made between 1.27° and 3.80°K. Above about 2°K the critical field curve is not parabolic. The experimental data satisfy the relationship $M^nT_c=$const if n is 0.46±0.02. The comparative impurity of the separated isotopes may be responsible for the low value of the exponent of M. The data for all the isotopes could be fitted by the curve

$$H_c=H_0(1.000-1.083t^2-0.0659t^4+0.349t^6-0.216t^8).$$

In a second paper, Maxwell (M3) reported on a more detailed study of the critical field curves for six specimens of different average isotopic mass. A ballistic method was used for the detection of superconductivity. The specimens were in the form of long wires and were either single crystals or consisted of a few large crystals. Maxwell took the critical field to be the value at which the specimen became completely normal. Hence, for a given field, the transition temperatures should be somewhat higher than those reported by other experimenters. A summary of Maxwell's data is given in Table III. The measurements were made at temperatures between 1.4° and 3.8°K. The threshold field curves were found to be geometrically similar to 1 part in 800 and definitely not parabolic above 2.7° or 3.0°K. The initial slope of the critical field curves was 147 oersted/deg and was the same to within 4 percent for all six specimens. The

TABLE III. Experimental results of Maxwell on separated isotopes of Sn.

M	Chem. purity exceeded	T_c (°K)	H_0 (oer)	H_0/T_c (oer/deg)
113.58	99.58%	3.808	312.59	82.06
116.67	99.69	3.771	...	...
118.05	99.19	3.744	307.70	82.21
118.70	99.996	3.742		
119.78	99.90	3.724		
123.01	99.91	3.667	300.97	82.16

calculated value of γ is 4.46×10^{-4} cal/mole deg^2. It follows from the data that $M^nT_c=$const with $n=0.505\pm0.019$.

LANTHANUM

The superconductivity of La was discovered by Mendelssohn and Daunt (M4). They used a magnetic method to detect the transition. Since their specimen was only about 98 percent pure, their measured values of 4.71°K for the transition temperature and greater than 1000 oersted/deg for the initial slope of the threshold field curve are probably not very accurate.

According to Shoenberg (S5) La becomes superconducting at 4.2°K and the critical fields are large.

Ziegler (Z1) used a magnetic method to determine the transition temperature of two specimens. One sample, containing 0.8 percent Fe had T_c equal to 4.85°K. A second sample, which contained up to 1 percent Al, S, and W, had a transition at 4.45°K.

A calorimetric determination of the specific heat was made by Parkinson, Simon, and Spedding (P1). The specimen they used was about 99.95 percent pure. At room temperature both hexagonal close packed and cubic close packed crystal structures were present. They suggested that the fact that La can exist in both forms with varying proportions may account for the widely different figures for T_c which have been reported. Parkinson, Simon, and Spedding found that the transition to the superconducting state occurred at 4.37°K. Below this temperature the specific heat was given by $c=4.5\times10^{-4}T^3$ cal/mole deg. Above 4.37°K they found $c=0.0016T+0.00020T^3$ cal/mole deg. Above 6° this curve falls below the experimental points. From the thermodynamic relations for superconductors one calculates an initial slope of the critical field curve of 280 oersted/deg.

James, Legvold, and Spedding (J2) determined the transition temperatures of two specimens by measuring the resistances. The iron content of one specimen was 4200 parts per million; in the other it was 85.5 ppm. Other impurities, largely Mg, were present in total amount less than 1 percent. The first specimen was cast and then annealed at 600°C for 19 hours. The second specimen was extruded and not annealed. Annealing did not seem to have a predictable effect on the transition temperature or on the temperature spread of the transition. The measured values of T_c ranged from 5.5° to 6.0°K depending on the specimen and also on the heat treatment. The temperature width of the transition varied from 0.3° to 0.9°. The amounts of the two crystalline modifications present differed in the two samples and also, perhaps, as a result of heat treatment [see reference (Z2)].

Ziegler, Young, and Floyd (Z2) studied the transition of La between the hexagonal close packed and the face-centered cubic structures and also the superconducting transition. They had six samples available, three of which were rather impure (~95 percent). The other three specimens had purities which may have been as high as 99.7, 99.9, and 99.0 percent. When these specimens were received they were in the hexagonal close packed modification. The superconducting transition temperatures ranged from 3.1° to 5.45°K and the transition range was from 0.1° to 0.30°. After heating for 4 days at 350°C (and for one specimen for 4 days at 700°C) all but one of the specimens had the face centered cubic structure. For the three least pure specimens the superconducting transition temperatures after heat treatment lay between 3.2 and 5.25°K. For the purest specimens T_c lay between 5.3 and 5.5°K. The transition range was somewhat greater than before.

Ziegler, Young, and Floyd concluded from their measurements that both the face centered cubic and hexagonal close packed modifications are superconducting, the transition temperatures being 5.4°K and >3.9°K, respectively.

HAFNIUM

Hafnium possibly has the lowest transition temperature of all pure superconducting elements. The superconductivity of Hf was first discovered by Kurti and Simon (K9). Their experimental arrangement is discussed above under Zr. The Hf specimen used was in the form of a rod about 1 cm long and 2 mm in diameter. No estimate of the purity was given. The transition was found to occur at a magnetic temperature of 0.35 ± 0.05°K.

Smith and Daunt (S10) used a Hf specimen of 98.9 percent purity which contained about 0.9 percent Zr. It was in the form of a wire 50.5 mm long and 3.4 mm in diameter. The wire was pressed into a pill with powdered potassium chrome alum by applying a pressure of 5000 lb/in^2. The unannealed specimen showed no signs of superconducting behavior down to 0.15°K. After annealing for three hours at 900°C, a transition was observed to occur at 0.374 ± 0.01°K. The specimen was still very hard and the magnetic behavior not reversible. The initial slope of the critical field curve was observed to be about 230 oersted/deg; the measurements extended only to 0.312°K. Since annealing seems to make such a profound difference in the superconducting behavior, it would be very interesting to have more experimental data on Hf.

TANTALUM

Mendelssohn and Moore (M5) determined the threshold field curve for a Ta wire of unstated purity by measuring the resistance. They also measured the induction in a Ta sphere and two Ta rods. The purity of the specimens used in the induction experiments ranged up to 99.9 percent. The transition temperatures were 4.0°–4.4°K and the initial slopes of the threshold field curves lay between 1000 and 2000 oersted/deg. The results differed from specimen to specimen, but in each case characteristic alloy behavior was found.

Daunt and Mendelssohn (D5) used a Ta rod whose purity exceeded 99.95 percent. A magnetic method was used for detection of superconductivity. From the data and curves given in their paper one can infer that T_c was about 4.4°K and $(dH_c/dT)_{T=T_c}$ was approximately 320 oersted/deg.

Daunt, Horseman, and Mendelssohn (D4) deduced from the data of Daunt and Mendelssohn that H_0 was 1000 oersted and that the electronic specific heat was $19\times10^{-4}T$ cal/mole deg^2. Since Ta is a hard superconductor, and since the specimen probably was not annealed, it seems unlikely that these values of T_c and H_0 are characteristic of the pure metal. Also, the calculated value of the electronic specific heat may be inaccurate. It is, however, of the order of magnitude which one expects for a transition metal.

Keesom and Désirant (K2) carried out calorimetric measurements on a specimen whose purity exceeded 99.9 percent. They give no information concerning heat treatment of the specimen so it is reasonable to assume it was not annealed. Their measurements extended from about 1.4° to 4.8°K. In the normal state the specific heat was found to be

$$[464.5(T/264.5)^3-0.00141T] \text{ cal/mole deg.}$$

In the superconducting state the specific heat was proportional to T^3, the Debye characteristic temperature being 113°K. T_c was found to be about 4.06°K. Several values of the critical field were computed from the calorimetric measurements. The calculated initial slope of the threshold field curve was of the order of 1200 oersted/deg.

Webber (W1) attempted to determine the effects of annealing and gas content on the superconductive properties of Ta. He made resistance measurements on wires taken from the same spool but subsequently subjected to different heat treatments. One specimen was untreated. The observed T_c was 4.156°K and $(dH_c/dT)_{T=T_c}$ was 1360 oersted/deg. A second specimen was kept in a vacuum while being heated to 2200°–2500°C for 2 hours by the simple expedient of passing a current through it. The transition temperature was raised to 4.30° and $(dH_c/dT)_{T=T_c}$ decreased to 600 oersted/deg. A third specimen was heated like the second in a vacuum but then allowed to absorb air for a few minutes at 1200°C and 10^{-3} mm Hg pressure. Its behavior above 3° was the same as that of the second specimen. Webber concluded that the effect of the gas was slight, but the evidence can hardly be regarded as conclusive since it is not certain that the specimens were ever completely outgassed. Webber did, however, show clearly that the heat treatment of the specimen is important in determining the superconducting behavior.

The experiments of Preston-Thomas (P4) were on wires of unstated purity which were annealed by heating to 2800°K for 100 hours in a high vacuum. Resistance and induction measurements were made. Although no figures are given, it appears from the graphs that $T_c\sim4.5$°K and $H_0\sim840$ oersted. The initial slope of the critical field curve was less than 400 oersted/deg, the smallest value yet reported for Ta. The measurements of Preston-Thomas extended from 1.7°K up to T_c (and on to 300°K).

Heat capacity measurements have been made by Worley, Zemansky, and Boorse (W5) on two specimens whose purity exceeded 99.9 percent. Both specimens were vacuum annealed at a temperature of about 1000°C. The trasitions were found to occur between 4.01° and 4.42°K in one specimen and between 4.36° and 4.40°K in the other. In the normal state and at temperatures down to about 3°

$$c_n=\gamma T+(464.4/\Theta^3)T^3$$

with γ equal to 13.1 and 12.1×10^{-4} cal/mole deg^2 and Θ equal to 225° and 213° in the two specimens.

These data were subsequently recalculated (R. Worley, private communication). The values of γ were found to be 13.6 and 13.0×10^{-4} cal/mole deg^2 while the revised values of Θ are 237° and 230°K.

RHENIUM

The superconductivity of Re was first reported by Aschermann and Justi (A4). They made resistance measurements on a sintered powder specimen and observed a transition at about 0.9°K. Their results were not generally believed for many years because the resistance method is not a reliable indicator of the superconductivity of the dominant component of an impure specimen and because of the position of Re in the periodic table.

Daunt and Smith (D6) used a ballistic mutual inductance method to search for the transitions. Their specimen was a powder which had a purity of 99.8 percent. It was annealed in vacuum at 800°C for $2\frac{1}{2}$ hours. The measurements extended from 2.12°K to the transition temperature which was found to be 2.42°K. The initial slope of the threshold field curve was 235 oersted/deg. The observed transitions were rather broad; this fact was attributed by Daunt and Smith to the irregularly shaped particles of the specimen. The value of γ calculated from the threshold fields is 4.6×10^{-4} cal/mole deg^2.

Hulm (H3) prepared a solid Re rod whose impurity content was less than 0.01 percent. Resistance and threshold field measurements were made. The transitions were sharp. The zero-field transition temperature was found to be 1.699°K and the threshold field curve to be parabolic with $H_0=0.88$ oersted. According to Hulm, untreated powder specimens had transitions which were spread over the temperature range 1.7 to 2.4°K. After compression and annealing of these specimens at 1460°C for 12 hours, the transition region was reduced to 1.7 to 1.8°K. Hulm suggests that the high transition temperature reported by Daunt and Smith

TABLE IV. Experimental results of Reynolds, Serin, Wright, and Nesbitt on separated isotopes of Hg.

M	T_c (ref. R2)	T_c (ref. S3)	$M^{\frac{1}{2}}T_c$ (ref. S3)
203.4	4.126	4.137	58.88
202.0	4.143	4.147	58.84
200.7	4.150	4.154	58.93
199.7	4.161	4.167	58.99

was due to the existence in their powder specimen of appreciable amounts of very fine particles.

OSMIUM

Goodman (G1) used an ac susceptibility method for the detection of superconductivity. He found that the critical field curve for Os is parabolic with T_c equal to 0.71°K and H_0 equal to 65 oersted. No details concerning the specimen are given.

MERCURY

The great advantage of working with Hg is that it can be easily prepared in a state of very high chemical purity. Some care must, however, be taken in order to prepare specimens which are free of strains.

The experiments of Daunt and Mendelssohn (D5) were on a spherical specimen of high but unspecified purity. A ballistic mutual inductance method was used to detect the transition which was found to occur at 4.2°K in zero magnetic field. The threshold field curve was determined down to 1.5°K. From these data Daunt, Horseman, and Mendelssohn (D4) calculated that the critical field at absolute zero was 400 oersted. The initial slope of the threshold field curve was 190 oersted/deg and the calculated value of γ was 3.8×10^{-4} cal/mole deg^2.

Misener's (M6) experiments were on a long cylinder cast in a thin glass capillary. Its purity was 99.999 percent. A magnetic method was used for detecting the transitions to the superconducting state. The zero-field transition temperature was found to be 4.167°K (1937 scale). The critical field curve, determined by fitting a polynomial to the data, has the form

$$H_c=412.58-19.50T^2-2.133T^3+0.266T^4.$$

The value of H_0 was 412.58 oersted and the electronic specific heat calculated from these data was $4.5\times10^{-4}T$ cal/mole deg. In the superconducting state the calculated specific heat was proportional to T^3.

Pickard and Simon (P2) measured the specific heat calorimetrically in the range 3.5°K to 90°K. They did not analyze their data into a Debye-type term and an electronic term. In fact, it appears from their plotted data that such an analysis is not possible in the range of measurement. It is stated that the specific heat is anomalously high at low temperatures.

Recent studies of the superconductivity of Hg have been directed toward making precise measurements on different isotopes.

Maxwell (M1) used a natural specimen whose average isotopic mass was 200.7 and a sample of 98 percent isotopically pure Hg^{198}. The transitions were found to occur at 4.156° and 4.177°K (1949 scale) in the two specimens.

Reynolds, Serin, Wright, and Nesbitt (R2) used an ac inductance method to determine the transition temperatures of several Hg isotopes. The specimens were wires. The results given in Table IV were obtained. The initial slope of the critical field curve was found to be 204±2 oersted/deg.

In a second note, Serin, Reynolds, and Nesbitt (S3) revised the transition temperatures to a certain extent and also showed that $M^{\frac{1}{2}}T_c$ was approximately constant for the different isotopes. They state that the threshold field curves were accurately parallel down to 2.30°K.

In their third note Serin, Reynolds, and Nesbitt (S4) state that measured transition temperatures for the original samples plus three other of slightly different isotopic constitution could be fitted by the curve $T_cM^{0.504}=\text{const.}$

A more complete report on this work was published by Reynolds, Serin and Nesbitt (R1). The samples were purified by double and triple distillation and were prepared by sealing the Hg under He gas in glass capillaries. An ac inductance method was used to detect the transitions. Most of the measurements were made between 4.0° and 4.2°K. However, twice the critical field measurements were extended to 1.7°. Within experimental error the critical field curves were found to be parabolic. Some of the data are given in Table V.

In this table, K is the coefficient of the cubic term in the usual expression for the lattice specific heat. In view of the rather restricted temperature range in which most of the critical field data were collected, not too much reliance should be placed on the extrapolated values of H_0. The relationship between the isotopic mass and the transition temperature was found to be $T_cM^{0.504}=\text{const.}$

THALLIUM

Keesom and Kok (K4 and K5) measured the specific heat of Tl by a calorimetric method between 1.3° and 4.2°K and also the latent heat of transition. A 731-gram block of unspecified purity was used. If one can judge by the scatter of the experimental points, the accuracy was not very high. The transition temperature appears to have been at about 2.36°K. Below T_c, the Debye characteristic temperature was approximately 78.5°K. The data for temperatures higher than T_c were not

TABLE V. Experimental results of Reynolds, Serin, and Nesbitt on separated isotopes of Hg.

M	T_c (°K)	H_0 (oersted)	γ (cal/mole deg^2)	K (cal/mole deg^4)
199.5	4.185	420	3.82×10^{-4}	6.52×10^{-6}
200.7	4.173	419	3.82	6.57
202.0	4.159	417	3.82	6.65
203.2	4.146	414	3.80	6.65

analyzed into a Debye term plus a term linear in T. In their second paper Keesom and Kok give data on the specific heat in a magnetic field.

Daunt, Horseman, and Mendelssohn (D4) used a specimen in the form of a sphere cast *in vacuo*. It was 99.995 percent pure. A magnetic method was used for the observation of the transitions. T_c was found to be about 2.4°K and H_0 (extrapolated) to be 170 oersted. The calculated value of γ was 2.8×10^{-4} cal/mole deg^2.

Misener's (M6) specimen was a long wire cast in a glass capillary. Its purity was 99.995 percent. Magnetic measurements were made and a least squares method used to fit a polynomial to the observed critical field curve. The following result was obtained:

$$H_c=170.67-30.93T^2-0.193T^3+0.219T^4.$$

The transition temperature in zero field was 2.392°K (1937 scale). The value of γ deduced from the data was 3.4×10^{-4} cal/mole deg^2. Misener states that the specific heat in the superconducting state varied as T^3.

LEAD

Experiments on lead are facilitated by its easy availability and because it can be prepared in a state of high purity. Unfortunately, the experiments themselves are not so easy to perform. The chief reason is that the transition temperature is about 7°K which is well out of the liquid helium temperature region. The critical fields are rather high but no great difficulties are involved in producing them.

The experiments of Daunt and Mendelssohn (D5) were on a lead sphere cast *in vacuo*, the material having a purity in excess of 99.999 percent. The measurements, by a magnetic method, extended from 1.5° to 4.2°K. Because of the restricted temperature range it is difficult to derive reliable values of T_c or H_0 from their data. The measurements were, however, extended by Daunt, Horseman, and Mendelssohn (D4) to 6.85°K. From the combined data the following values were determined: $T_c=7.2$°K (1932 scale), $H_0=800$ oersted, and $\gamma=7.0\times10^{-4}$ cal/mole deg^2.

Justi (J3) attempted to observe an isotope effect in Pb. As Kamerlingh Onnes and Tuyn had done earlier, he used two specimens, one of natural lead and one composed of lead derived from the radioactive decay of U. He was unable to detect any significant difference in the transition temperatures.

The first successful attempt to observe an isotope shift in the transition temperature of Pb was made by Olsen (O1). She had available two samples of average isotopic mass 206.15 and 207.72. A resistance measuring technique was used to determine the values of T_c. They were found to differ by 0.038° and to be slightly higher than 7.2°K. The relation $M^{0.73}T_c=$const fits the experimental data.

A somewhat more extensive series of measurements was made by Serin, Reynolds, and Lohman (S2). Unfortunately all their data were taken at temperatures between 1.6° and 4.2°K. For the two purest specimens (99.998 percent and 99.88 percent) the difference of the critical fields was 5.1 ± 0.5 oersted and was independent of temperature. This difference is more than twice as large as that calculated by assuming $H_0M^{\frac{1}{2}}=$const but is consistent with the work of Olsen. An ac inductance method was used in the determination of the critical fields.

The isotope shift in lead should probably be investigated further since most other experimental and theoretical evidence indicates that $T_cM^{\frac{1}{2}}=$const or $H_0M^{\frac{1}{2}}=$const.

Preston-Thomas (P3) made measurements on lead of spectrographic purity which was cold extruded into a wire. The magnetic transitions were found to be approximately discontinuous while the resistive transitions were spread out. No data concerning T_c or the critical fields are given by him.

Clement and Quinnell (C3) measured the specific heat in the vicinity of T_c. Their specimen was 99.996 percent pure. A discontinuity is present, as one expects. They give the following table:

T(°K)	c_s-c_n (cal. exp.)	c_s-c_n (mag. calculated)
6.75	0.0104 cal/mole deg	0.0096 cal/mole deg
7.00	0.0117	0.0112
7.23	0.0126	0.0126

From the figure which accompanies Clement and Quinnell's paper it appears that the specific heat is a linear function of T in the range of measurement (6.75°–7.75°K).

Horowitz, Silvidi, Malaker, and Daunt (H2) made calorimetric measurements between 1° and 75°K. Their specimen was 99.99 percent pure. In the normal state at sufficiently low temperatures they found that the lattice specific heat was proportional to T^3 with a Debye characteristic temperature of 96.3°K and that the electronic specific heat was $7.48\times10^{-4}T$ cal/mole deg. A value $5.00\times10^{-5}T^3$ cal/mole deg was obtained for the electronic specific heat in the superconducting state by subtracting from the measured value the lattice specific heat corresponding to $\Theta=96.3$°K.

THORIUM

Shoenberg (S6) used a ballistic method to determine the threshold field curve of thorium. The transition temperature reported in his first communication is 1.32°K, and he states that the initial value of dH_c/dT is high.

Subsequent measurements by Shoenberg (S7) on another specimen, presumably purer, yielded $T_c=1.368$°K (1932 scale) and a value 191 oersted/deg for $(dH_c/dT)_{T=T_c}$. The measurements were made between 1.0° and 1.35°K.

URANIUM

There has been considerable uncertainty as to whether or not uranium is a superconductor, but it now seems established that it is.

TABLE VI. Transition temperatures, critical fields, and electronic specific heats of the superconducting elements. The spread of the measured values is indicated and the most likely values printed in boldface type.

Element	Crystal structure	T_c (°K)	H_0 (oersted)	γ mag (cal/mole deg^2) $\times 10^4$	γ cal (cal/mole deg^2) $\times 10^4$
Al	fcc	1.13–**1.197**	**106**	2.59–**2.95**	**3.484**
Ti	hcp	**0.387**–0.56	**20**–130	**1.1**	**8.00**
V	bcc	4.69–**4.89**–5.13	**1120**–10 000	**15.0**	**21.1**–21.9
Zn	hcp	0.84–**0.905**–0.96	42–**52.5**	**1.16**–1.36	1.25–**1.50**
Ga	tetr	1.06–**1.103**	47–**50.3**	**0.91**	
Zr	α hcp β bcc	**0.546**–0.70	**46.6**–140	**3.92**	**6.92**
Nb	bcc	8.35–**8.70**–8.85	**1960**–8250		**21**
Tc		**11.2**	300–400		
Ru	hcp	**0.47**	**46**		
Cd	hcp	0.54–**0.560**–0.65	27–**28.8**–33.8	**1.28**–1.54	**1.70**
In	tet f.c.	3.37–**3.396**–3.40	269–**278**	3.5–**4.3**	4.0–**4.33**
Sn	tetr	3.702–3.752	304–310	3.95–4.46	**4.0**
La	α hcp β fcc	4.2–**5.4**–6.0			**16**
Hf	hcp	**0.37**			
Ta	bcc	4.06–**4.38**–4.5	900–2800	19	**12.1**–14.1
Re	hcp	0.9–**1.699**–2.42	**188**–285	**4.1**–4.6	
Os	hcp	**0.71**	**65**		
Hg	rhomb	4.150–4.173	400–419	3.8–4.5	
Tl	α hcp β fcc	2.36–**2.392**	**171**	2.8–3.4	
Pb	fcc	**7.2**	**800**	**7.0**	**7.48**
Th	fcc	**1.37**	**131**		
U		0.8–1.3			

Shoenberg (S7) first found that two specimens were not superconducting down to about 1°K but one of them seemed to contain about 3 percent by volume of superconducting material below 1.1°. A ballistic method was used for the detection of superconductivity.

Aschermann and Justi (A4) found, on the basis of resistance measurements, that U becomes superconducting at about 1.3°K. According to Shoenberg's (S8) later measurements, however, a very pure specimen was not superconducting down to 1.08°K. Alekseyevsky and Migunov (A1) reported that U became superconducting below 1.3°K. According to them less pure specimens were not superconducting.

Goodman and Shoenberg (G3) confirmed that U is a superconductor but found that the specimen of highest purity tested had the highest T_c. About all one can say for sure is that T_c depends markedly on the purity. Goodman and Shoenberg also found that the fields necessary to destroy superconductivity were of the order of 2000 oersted. They state that the results of some specific heat measurements make it unlikely that these are true critical fields. The same conclusion can perhaps be drawn from the high values of the critical fields or from the strong dependence of T_c on the purity of the specimen.

SUMMARY

Some of the experimental results are summarized in Table VI. An attempt has been made to select the most reliable data, which are given in boldface type, and to indicate the range within which the measured values fall.

It is clear from Table VI that the results of different experimenters are not in very good agreement. In the case of the hard superconductors, where T_c and H_0 depend markedly on the physical and chemical purity of the specimens, a certain spread in the experimental values of these quantities is to be expected. However, for the soft superconductors it seems that the agreement should be better than it generally is. The differences in the results obtained by the various observers can be ascribed in part to thermometric technique and to the methods of specifying T_c and H_0. It seems desirable to adopt a conventional method for the specification of the threshold field and temperature.

A second fact which emerges from inspection of Table VI is that, except for Sn and the dubious case of Ta, the values of γ determined from the threshold field curves are lower than the values determined calorimetrically. Part of the difference may result from the fact, pointed out by Clement and Quinnell, that γ_{mag} is sensitive to the assumption made about the analytical form of the threshold field curve.

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