Superconductivity of the Isotopes of Tin*

E. MAXWELL
National Bureau of Standards, Washington, D. C.
(Received December 26, 1951)

The superconducting transition temperatures of six samples of tin with masses ranging from 113.58 to 123.01 were measured by a magnetic method and found to obey a relation of the form $M^{0.505}T_c = $ const. The critical field curves for the samples of mass 113.58, 118.05, and 123.01 were determined between 1.4°K and 3.8°K and observed to be geometrically similar to about 1 part in 800. From this it is concluded that the electronic specific heat in the normal state is independent of mass, and that the thermodynamic functions derived from the critical field curves also have the similarity property.

I. INTRODUCTION

THE possible existence of an isotope effect in superconductivity was first explored by Kamerlingh-Onnes and Tuyn,[1] and again almost twenty years later by Justi.[2] These investigators looked for differences in the transition temperatures of ordinary lead (atomic weight 207.22) and uranium lead (atomic weight 206.15), but reported negative results. Since the transition of lead occurs at 7.2°K, a region in which precise determination and regulation of the temperature is difficult, it was considered worthwhile to re-examine the question at the National Bureau of Standards using some of the pure mercury isotope 198.[3] Its transition temperature was found to be about 0.02°K higher[4] than natural mercury (atomic weight 200.6). At about the same time, Reynolds, Serin, Wright, and Nesbitt[5] independently found similar shifts in the transition temperature for some samples of mercury enriched in isotopes of mass 199, 202, and 204, respectively.

In view of the fact that the earlier investigators had reported negative results for lead it was important to ascertain whether or not the effect was common to all superconductors or a special property of mercury alone. Accordingly, several samples of enriched isotopes of tin and thallium were obtained from the Atomic Energy Commission, and the existence of the isotope effect was verified for these metals as well. Some of the preliminary results have been reported elsewhere.[6-8] More recently the isotope effect was observed in lead also by Olsen[9] and by Reynolds and Serin.[10] It now appears that the earlier negative results of Kammerlingh-Onnes and Justi were perhaps due to insufficient resolving power in temperature.

It was shown by Reynolds, Serin, and Nesbitt[11,12] that the data for mercury could be approximately represented by the relation $M^{\frac{1}{2}}T_c = $ constant. Furthermore, theoretical treatments by Fröhlich[13] and Bardeen[14] appeared, which were based on interaction between electrons and lattice vibrations and which specified that $T_c \sim M^{-\frac{1}{2}}$. (Fröhlich had developed his theory prior to his knowledge of the isotope effect.) In view of these developments tin appeared to be worth careful study, since the range of stable isotopes was large (112–124) and since for many purposes it was a more ideal material to work with than mercury. (The difficulty of realizing strain-free mercury specimens had complicated the problem of making precise measurements.) The present paper is an account of the critical field measurements thus far completed on tin isotopes.

II. EXPERIMENTAL DETAILS

The critical field measurements were made by observing the magnetic transitions of the capillary wire specimens in a longitudinal magnetic field. The general features of the apparatus are shown in Figs. 1 and 2. The method depends on the change in magnetic susceptibility of the specimen when it passes from the superconducting to the normal state and makes use of a ballistic type of flux measurement. The specimen is located inside a pick-up coil and the change in flux threading the coil is observed when the magnetic field is interrupted. A null method is employed in which the change of induction in the pick-up coil is balanced by an equal change in induction through a set of compensating coils. The final balancing is done with a variable mutual inductometer.

The apparatus is designed to accommodate six samples, each with its own pick-up coil. In practice, anywhere from three to five samples were used in any one experiment, and one of the unused pick-up coils was employed as a fixed compensating coil.

* Supported by the ONR.
[1] H. Kamerlingh-Onnes and W. Tuyn, Leiden Communications No. 160 (1922).
[2] E. Justi, Z. Physik. **42**, 325 (1941).
[3] The suggestion of looking for a mass dependence in superconductivity was also made independently to us by Professor K. F. Herzfeld.
[4] E. Maxwell, Phys. Rev. **78**, 477 (1950).
[5] Reynolds, Serin, Wright, and Nesbitt, Phys. Rev. **78**, 487 (1950).
[6] E. Maxwell, Phys. Rev. **79**, 173 (1950). See also references 17, 18, and 19.
[7] E. Maxwell, Proc. Natl. Bur. Standards Symposium on Low Temperature Physics, March 27–29, 1951 (to be published).
[8] E. Maxwell, Report on Conference for Very Low Temperature Physics, Oxford, England, August 22, 1951.
[9] Marianne Olsen, Nature **168**, 246 (1951).
[10] Reported by C. A. Reynolds at Conference for Very Low Temperature Physics, Oxford, England, August 22, 1951.
[11] Reynolds, Serin, and Nesbitt, Phys. Rev. **78**, 813 (1950).
[12] Serin, Reynolds, and Nesbitt, Phys. Rev. **80**, 761 (1950).
[13] H. Fröhlich, Proc. Phys. Soc. (London) **A63**, 778 (1950); also Phys. Rev. **79**, 845 (1950).
[14] J. Bardeen, Phys. Rev. **79**, 167 (1950); **80**, 567 (1950).
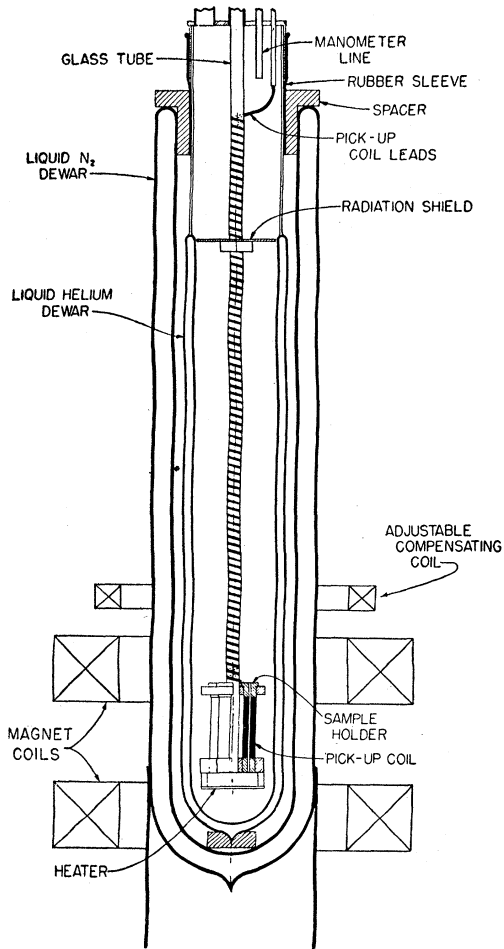
FIG. 1. Cross section of apparatus used for
determining critical fields.

The technique of measurement was as follows: The temperature was held constant and the magnetic field set to the desired level by adjusting the magnet current. The circuit was then balanced by adjusting the variable mutual inductance M until no deflection was observed on the ballistic galvanometer when the magnet current was interrupted. In this way the change in mutual inductance between the magnet and the pick-up coil could be observed as the specimen went from the superconducting to the normal state. The change was of the order of 40 to 100 μh with the specimens used in these experiments.

In some of the earlier measurements a deflection method was employed in which the system was balanced when the specimen was either in the normal or the superconducting state and the galvanometer deflection recorded at all other points in the transition. This method is somewhat more rapid, but not as precise as the null method. Except where otherwise noted, the data reported here were taken by the null method.

For measurements in weak fields, where maximum

sensitivity was desired, the ballistic galvanometer was a Leeds and Northrup type 2285x which had a period of 7 sec, resistance of 32 ohms, and a critical damping resistance of 110 ohms. The over-all sensitivity of the apparatus was of the order of 2000-mm deflection per cgs unit of magnetic moment. The short time zero instability was less than 0.1 mm. In strong fields where sensitivity was not important it was convenient to use a Leeds and Northrup type 2290 galvanometer with a 37-sec period. Since this galvanometer was highly overdamped in the circuit arrangement used, it was essentially a fluxmeter and eliminated "double-kicks" which were a nuisance whenever the shorter period galvanometer was used for strong field measurements. The "double-kicks" were caused by the fact that the voltage pulses induced in the sample and compensating coils had slightly different shapes so that as a balance was approached the galvanometer deflected first in one direction and then in the opposite because of its fast response. This made it difficult to decide when the system was balanced. With the fluxmeter the final deflection was proportional to the net change in flux and the balancing procedure greatly simplified. The sensitivity was, however, reduced by about a factor of five.

The pick-up coils were wound with 39,000 turns of No. 44 Formex wire on Bakelite forms and had a resistance of about 80 ohms at liquid helium temperatures. This resistance was about optimum for the shorter period galvanometer.

The Helmholtz coil magnet produced a field of 128.8 oersted/ampere which was homogeneous in the volume occupied by the samples to within 0.2 percent. All three components of the earth's field were balanced out by an auxiliary pair of Helmholtz coils to better than 1 milli-oersted.

Temperatures were measured by vapor pressure thermometry using the 1949 Mond Laboratory tables. A mercury manometer was used above 2.4°K, while below 2.4°K a butyl pthalate oil manometer was used
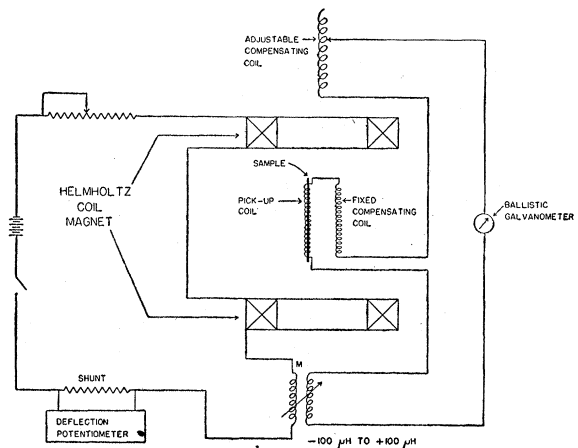

FIG. 2. Simplified circuit arrangement.

for greater sensitivity. The vacuum side of the oil manometer was continuously evacuated by a butyl pthalate diffusion pump. The oil manometer was frequently checked against the mercury manometer and gave results reproducible to ±0.1 mm oil. Corrections were made for the temperature variation of the density of the oil and mercury during all observations.

When working in the He I region, corrections were also made for the hydrostatic head of liquid helium above the samples. Because of the poor heat conductivity of He I the helium in the lower part of the Dewar can assume a slightly higher temperature than the liquid at the surface. The maximum temperature that can be assumed is that corresponding to the pressure of the vapor at the liquid surface plus the pressure head of the liquid column. (A heater was used at the bottom of the Dewar for stirring purposes which automatically insured that boiling took place at the lower end of the Dewar and fixed the temperature at the value determined by the hydrostatic head.) The head correction varied from a few thousandths of a degree at 4.2° to about 0.01° just above the lambda-point.

The tin isotopes were obtained from the Atomic Energy Commission in the form of SnO_2. These were reduced to the pure metal by heating in a hydrogen atmosphere.[15] The tin metal was then cast in the form of capillary wires by first melting the metal in vacuum, allowing the molten tin to flow into Pyrex capillaries and sealing off under vacuum. In order to prevent the wires from breaking up it was necessary to degas the molten tin as far as possible. This was done by running the molten metal in and out of the capillary several times. After about a dozen trials, enough gas would be removed so that the capillary wire would not be broken up by gas bubbles. The specimens were then remelted by placing the Pyrex capillaries in a furnace which was slowly raised up, allowing the samples to recrystallize as single crystals. Although no detailed examinations of crystal structure have been made, it seems reasonable that the wires are either single crystals or several large crystals.
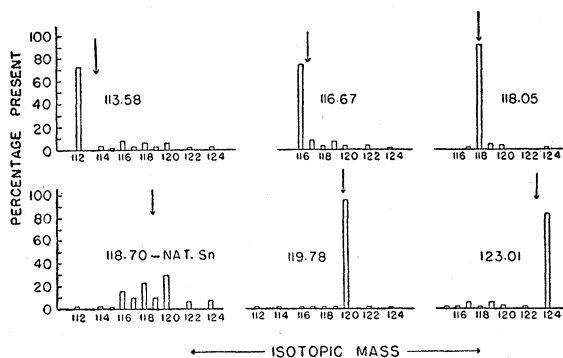

FIG. 3. Distribution of isotopic masses in the samples.

TABLE I. Critical field data for six samples of Sn.

Sample	Atomic mass[a]	Chemical purity	T_c °K 3–14–51	T_c °K 7–6–51	H_0	H_0/T_c
112–1	113.58±0.01	99.58[b]	...	3.8082	312.59	82.06
116–1	116.67±0.03	99.69[b]	3.7708	...	...	...
118–1	118.05±0.02	99.19[b]	3.7444	3.7440	307.70	82.21
Sn–2	118.70(nat.)	99.996	3.7419	...	...	...
120–1	119.78±0.05	99.90[b]	3.7238	...	...	...
124–1	123.01±0.08	99.91[c]	3.6669	3.6633	300.97	82.16

[a] The exact atomic masses of the individual isotopes were used in calculating the average masses of these samples.
[b] Oxide.
[c] Metal.

The isotopic purities of the samples are given in Fig. 3 and the chemical purities in Table I. The chemical purity refers to the state of the oxides as furnished by the AEC except as otherwise indicated. The reduction process probably reduced the impurity content, but no analyses of the metal itself are available except for the enriched Sn^{124} sample. The spectrochemical analysis of this sample showed less than 0.1 percent impurity content, so it is likely that the metals as finally refined were considerably purer than the analysis of the oxides indicated.

Since the critical fields for the different isotopes differed by only very small amounts, great emphasis was placed on precision in making the measurements. The general procedure used was to have from three to five samples in the apparatus during any one experiment and to observe the transition of each successively as the field was gradually increased, while the temperature was held constant. By this procedure the differences in critical field were determined rather more precisely than was possible for the absolute values themselves. This fact may be put to advantage by basing the detailed interpretation of the data on the differences $\Delta H(T)$ and ΔT_c, where $\Delta H(T)$ is the difference in critical field for a pair of isotopes as a function of temperature, and ΔT_c is the difference in zero-field transition temperatures.[16] A truly differential measurement to determine these quantities directly would be very desirable but was not feasible. An approach to this was made in the $\Delta H(T)$ measurement in which it was possible to determine the critical fields of the different samples in fairly rapid succession, so that temperature drifts were practically eliminated.

Since magnetic transitions always have a finite width and since the separation in critical fields between isotopes is small, the detailed interpretation of the transition curve is of some importance. The customary procedure in the past has been to take the half-point in the transition, the field at which the magnetic moment of the specimen has half of its maximum value. This, however, corresponds to a point in the intermediate state instead of the ideal phase equilibrium curve, and is moreover a function of the width of the transition curve, which in turn is governed by the
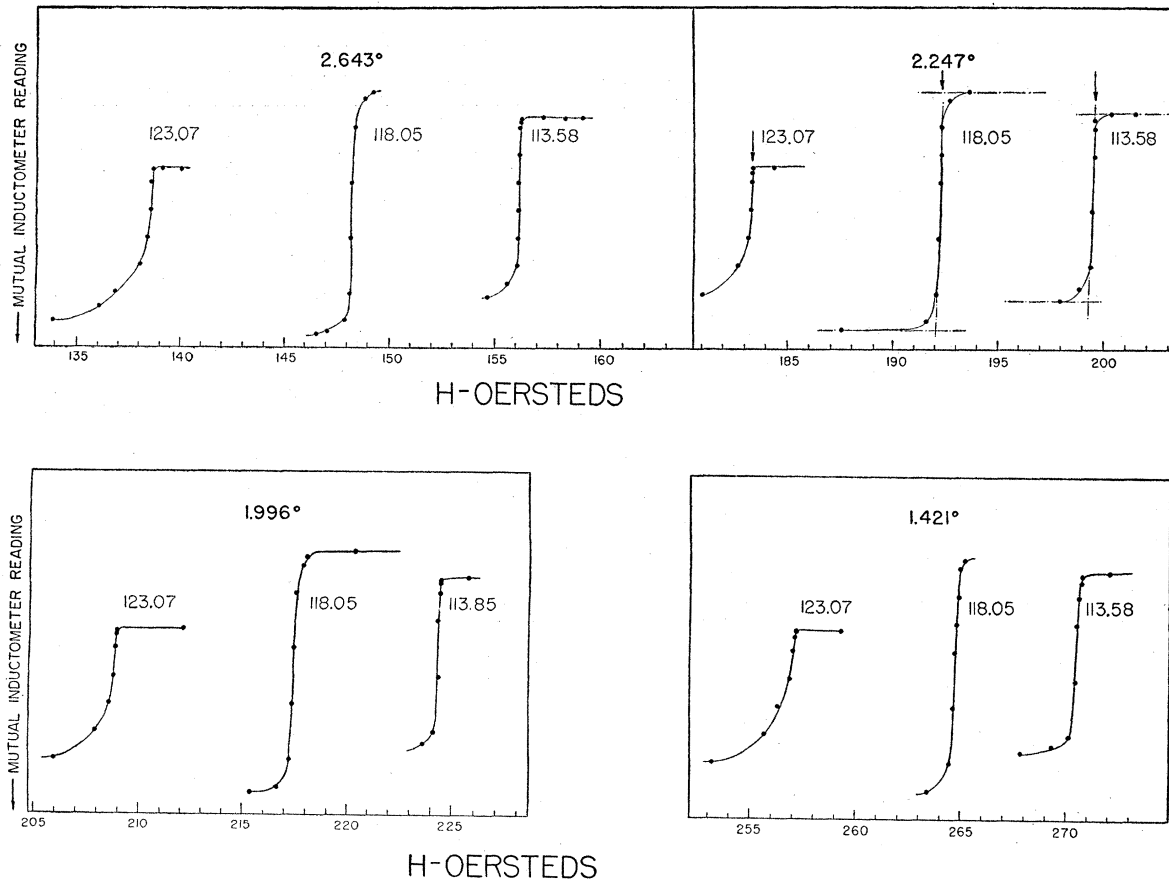
FIG. 4. Typical transitions at constant temperature. The method of selecting the equilibrium value of the field is illustrated in the data for 2.247°.

detailed geometry of the specimen. In this work the transition field was taken as the point at which the sample becomes completely normal, as interpreted by the arrows on the curve for 2.247° in Fig. 4. There is always a small amount of rounding to the curve on the high field side, the reason for which is not known, but is thought to be due to a secondary feature.

The rounding at the start of the transitions was interpreted as due to penetration of the field at the ends of the specimens due to the sharp edges. The length to diameter ratio of the specimens was of the order of 100:1, and consequently the effective demagnetization factor must have been the result of the effect of the sharp edges or other secondary features. The rounding was most noticeable in the sample of mass 123.07, which is somewhat irregular near the ends.

The procedure finally adopted was to trace out carefully each transition curve, point by point. It would normally take about fifteen to twenty minutes for each sample, so that for a group of three samples an hour might elapse between start and finish. As a check on slow drifts, a typical point on the steep part of each transition curve was selected and rapidly checked in succession on each of the three samples after all three

curves had been traced out at a given temperature. In this way the field differences could be accurately established. The errors in the differential field measurements are estimated to be less than 0.6 oersted at 1.4°K and somewhat lower at higher temperatures. This estimate is an upper limit which includes such factors as uncertainty in selecting the true critical fields from the transition curves and not merely the precision with which changes in the applied magnetic field could be measured, which was of the order of a few hundredths of an oersted.

The zero field transition temperatures were determined by taking a series of measurements in weak fields and extrapolating to zero field. Some of the transitions were observed in fields of the order of 1 oersted. Some of these samples were redetermined several times over a period of four months and showed shifts of only a few thousandths of a degree.

III. RESULTS

The critical field data observed in these experiments are summarized in Tables I and II and Figs. 5, 6, 9, and 10. The data in Table II were obtained using the null method described in Sec. II and are plotted in

Fig. 5. In Fig. 6 the data in the neighborhood of zero field are plotted to an enlarged scale. The diamond shaped points are observations made by the null method. The other points are earlier observations made by the deflection method in three different runs. The tails on the plotted points indicate the over-all widths of the transitions. The transition field is taken as the field at which the specimen becomes completely normal as interpreted in Fig. 4. The average slope at the transition temperature, $(dH_c/dT)_{T_c} = 147$ oersteds/°K, and is the same for all samples to within 4 percent.

The transition temperatures given in Table I are the intercepts of the curves of Fig. 6, and two separate sets of data are given corresponding to observations made on two different days. These are the best data. (The results of the other two sets of observations were incomplete and hence were not used.) For the purpose of finding the exponent in the mass-temperature relation, the two sets of data were considered separately, thus minimizing the effects of systematic errors.

The temperatures reported here are somewhat higher

FIG. 5. Critical field curves for tin isotopes.

TABLE II. Critical field data for Sn isotopes (field in oersteds).

T°K	$H_c(113.58)$	$\dfrac{H_c(113.58)}{-H_c(118.05)}$	$\dfrac{H_c(113.58)}{-H_c(123.01)}$
3.787	3.13	⋯	⋯
3.722	12.64	9.52	⋯
3.656	22.02	9.40	20.93
3.251	78.04	8.85	19.51
3.018	107.22	8.45	18.75
2.643	151.66	7.72	17.26
2.456	171.99	7.52	16.65
2.247	193.89	7.01	15.85
1.996	216.66	6.65	14.94
1.723	240.92	5.95	13.91
1.421	262.97	5.61	13.21
0(extrapolated)	312.40	4.89	11.62

than those reported by Lock et al.[17] and Bär et al.[18] on separated isotopes of tin but are consistent with those of Reynolds, Serin, and Nesbitt.[19] These divergencies may be due in part to differences in the purities of the materials, in part to systematic differences in thermometry and to differences in the method of selecting the critical fields. Except for the purity these considerations are of only secondary importance for the relative transition temperatures.

IV. INTERPRETATION

The critical field curves for the samples of mass 113.58, 118.05, and 124.01 are given in Fig. 5. These curves are definitely not parabolic, as may be seen in

[17] Lock, Pippard, Shoenberg, Allen, and Dawton, Nature 166, 1071 (1950). Also Lock, Pippard, and Shoenberg, Proc. Symposium on Low Temperature Physics, Natl. Bur. Standards, March 27, 1951 (to be published), and by the same authors, Proc. Cambridge Phil. Soc. 47, Part 4, 811 (1951).
[18] Bär, Mendelssohn, Olsen, Allen, and Dawton, Nature 166, 1072 (1951).
[19] Reynolds, Serin, and Nesbitt, Proc. Symposium on Low Temperature Physics, Natl. Bur. Standards (March 27, 1951) (to be published).
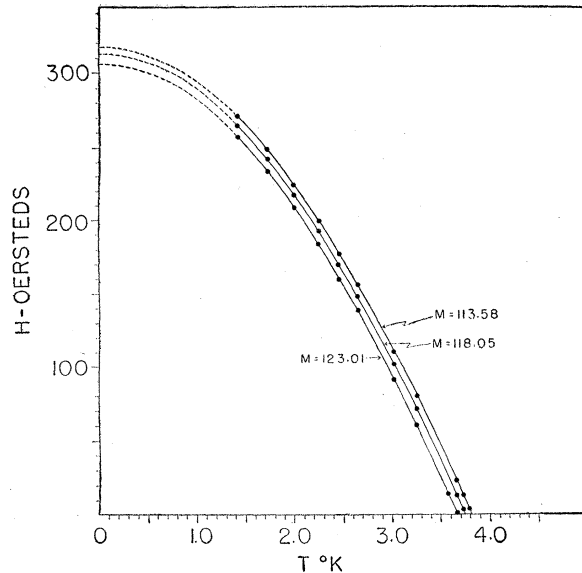
Fig. 7 where H is plotted against T^2 for the sample of mass 113.58. Although the parabola is a good fit below 2.7°K, it is clearly inadequate between 3°K and the transition temperature. It was found that the data could be nicely fitted by a three-constant equation, such as a hyperbola of the form

$$[(H_c - k)/a]^2 + (T/b)^2 = 1, \qquad (1)$$

or a cubic

$$H_c = H_0 - AT^2 + BT^3. \qquad (2)$$

For the sample of mass 113.58 the constants A, B, and H_0 in Eq. (2), determined by a least squares adjustment, were $A = 26.3445$, $B = 1.26076$, $H_0 = 312.593$. (It is convenient to carry six figures for computation purposes, although the last two are not physically significant.)
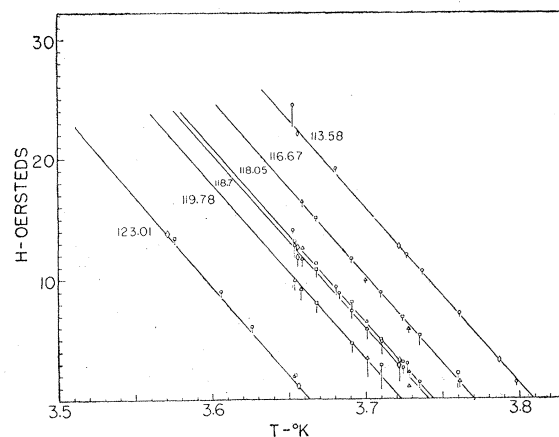

FIG. 6. Critical field curves for tin isotopes in small fields. □—data of March 14, 1951; △—data of April 17, 1951; ○—data of May 3, 1951; ◇—data of July 6, 1951. The points ◇ are probably most reliable. The vertical lines indicate the width of the transition.
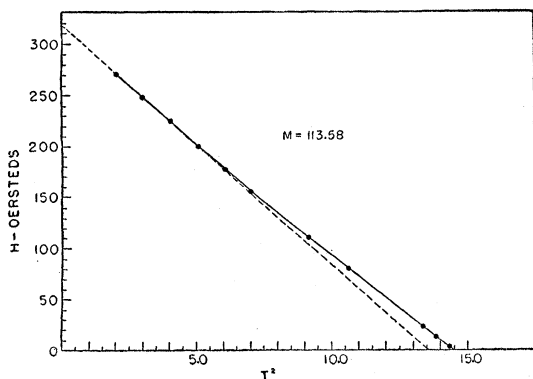
FIG. 7. Plot of H_c vs T^2 for tin sample with $M = 113.58$ showing departure from parabolic behavior.

Figure 8 is a deviation plot of the differences between the observed fields and those calculated from Eq. (2). The root-mean-square deviation is 0.27 oersteds. Adding higher order terms to the polynomial would have reduced the mean square deviation but was not done since it would also have imparted an oscillatory character to the critical field curve. The absolute value of the deviation was under 0.5 oersted and therefore within the estimated experimental error.

A preliminary trial with the hyperbola of Eq. (1) suggested that an equally good fit might be obtained. However the fitting of a hyperbola in the least squares sense was not attempted, since it would have involved much more labor and offered no special advantage.

The critical field curves of Fig. 5 are geometrically similar, i.e., they can be described by a universal critical field curve of the form

$$h_c = f(t), \qquad (3)$$

where $h_c = H_c/H_0$, $t = T/T_c$, and further H_0/T_c is the same for all curves. This is in agreement with Lock, Pippard, and Shoenberg.[17] As shown by them, the difference in critical fields for a pair of isotopes is a very sensitive test of geometrical similarity. This is advantageous since the differences in critical field are known more precisely than the absolute values of the field itself.

Let

$$H_{c1} = H_{01} - A_1 T^2 + B_1 T^3 \qquad (2a)$$

and

$$H_{c2} = H_{02} - A_2 T^2 + B_2 T^3 \qquad (2b)$$

be the equations of critical field curves for two samples of different atomic weight. If these two curves are geometrically similar in the sense of (3) then the difference in critical fields is given by

$$H_c = H_{c1} - H_{c2} = H_{01} \frac{\Delta T_{12}}{T_{c1}} + A_1 \frac{\Delta T_{12}}{T_{c2}} T^2$$

$$- B_1 \frac{\Delta T_{12}}{T_{c2}} \left(2 + \frac{\Delta T_{12}}{T_{c2}} \right) T^3, \qquad (2c)$$

where T_{c1} and T_{c2} are the transition temperatures of samples 1 and 2, respectively, and $\Delta T_{12} = T_{c1} - T_{c2}$. (Sample 2 is assumed to have the greater atomic mass.) Equation (2c) determines ΔH_c in terms of the observed zero field transition temperature difference ΔT_{12}. The test for geometrical similarity consists in comparing the observed values of ΔH_c with those computed according to Eq. (2c).

Figure 9 shows this comparison for $\Delta H(113.58, 123.01)$ and $\Delta H(113.58, 118.05)$, respectively. The agreement is considered good. The observed ΔH_c's lie somewhat below the calculated values at the lower end of the temperature scale, but the deviations are of the order of half an oersted and within the limit of error. For geometrically similar curves $\Delta H_0/H_0 = \Delta T/T_c$. $\Delta H_0/H_0$ is about 6 percent lower than $\Delta T/T_c$ for the pair 113.58–118.05, while for the pair 113.58–123.01 it is within 3 percent. This is about the correct order of magnitude to be accounted for by experimental error and indicates that the curves are geometrically similar to approximately one part in 800.

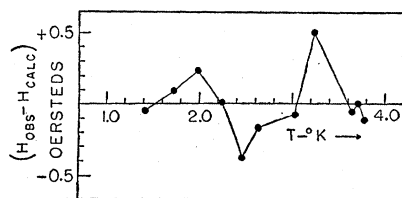Geometrical similarity implies that the ratio H_0/T_c is constant for the different isotopes. Fröhlich[13] and

FIG. 8. Deviations of observed critical field for $M = 113.58$ from the equation $H_c = 312.593 - 26.3445T^2 - 1.26076T^3$.

Bardeen[14] have predicted that $H_0 \sim M^{-\frac{1}{2}}$, as the result of theories based on interaction of electrons and zero-point vibrations, and consequently when geometrical similarity obtains $T_c \sim M^{-\frac{1}{2}}$. Figure 10 is a logarithmic plot of the data of Table I in which straight lines have been fitted separately to the two sets of data. These two determinations yield slopes of 0.487 ± 0.026 and 0.522 ± 0.028 (the precision indexes are the standard deviations) or a mean slope of 0.505 ± 0.019. The standard deviations give an indication of the internal consistency of the data, but it should be realized that the possible effects of purity, strain, and similar physical properties are unknown and are difficult to evaluate. Nevertheless it is clear that these results are highly consistent with the relation $T_c \sim M^{-\frac{1}{2}}$, and consequently lend support to the hypothesis that superconductivity is intimately associated with the interaction of electrons with zero point lattice vibrations.

If the reduced critical field is a universal function of the reduced temperature for all isotopes, as expressed by (3), it follows that the thermodynamic quantities which depend on the critical field can also be written as universal functions of the reduced temperature when properly normalized. The entropy difference, latent

heat, and specific heat difference per mole are given by

$$S_n - S_s = - (V_m/4\pi)H_c(dH_c/dT) \quad (4a)$$

$$Q = - (TV_m/4\pi)H_c(dH_c/dT) \quad (5a)$$

$$C_n - C_s = V_m\{(T/4\pi)H_c(d^2H_c/dT^2) \\ + (T/4\pi)(dH_c/dT)^2\}, \quad (6a)$$

where V_m is the molar volume. The corresponding reduced equations are

$$s_n - s_s = \frac{S_n - S_s}{H_0(H_0/T_c)} = - V_m \frac{h}{4\pi}\frac{dh}{dt} \quad (4b)$$

$$q = \frac{Q}{(H_0^2/8\pi)} = - 2th\frac{dh}{dt}V_m \quad (5b)$$

$$c_n - c_s = \frac{C_n - C_s}{T_c(H_0/T_c)^2} = V_m\left\{\frac{t}{4\pi}h\frac{d^2h}{dt^2} + \frac{t}{4\pi}\left(\frac{dh}{dt}\right)^2\right\}. \quad (6b)$$
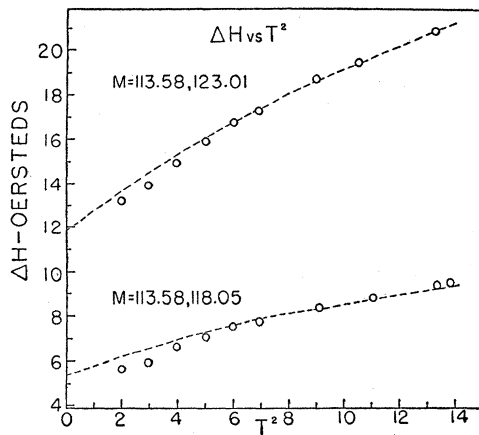

FIG. 9. Plot of ΔH_c vs T^2 for the pairs of tin samples with masses (113.58, 123.01) and (113.58, 118.05). Dotted curve calculated from Eq. (4).

In Eqs. (4b), (5b), and (6b), $h = H_c/H_0$ and $t = T/T_c$ are the reduced critical field and temperature. The quantities s, q, and c, defined as indicated in terms of S, Q, and C, are universal functions of h and t and apply to all the isotopes. This follows as a consequence of the similarity property.

The temperature dependence of the entropy and specific heat differences can be determined directly from the explicit relation for the critical field as per Eqs. (4) and (6). If $H(T)$ is given by a polynomial the entropy and specific heat differences will contain a linear term in T plus higher order terms. (For the case of a parabola[20-22] only linear and cubic terms are present.) The linear term is generally identified with the entropy or specific heat of the electrons in the normal state. The

[20] J. A. Kok, Leiden Communications 77a (1934).
[21] C. J. Gorter and H. Casimir, Physik. Z. 35, 963 (1934).
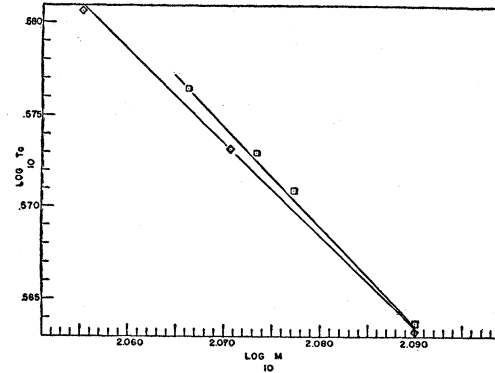[22] A. Sommerfeld, Z. Physik 118, 467 (1941).

FIG. 10. Plot of $\log_{10}T_c$ vs $\log_{10}M$ for tin isotopes. The best value of α in the formula $M^\alpha T_c = $ constant is $\alpha = 0.505 \pm 0.019$.

coefficient of the linear term is given by

$$\gamma = - \lim_{T\to 0}\frac{V_m}{8\pi}\frac{d^2H_c^2}{dT^2} = - \lim_{T\to 0}\frac{V_m}{8\pi}\frac{H_0^2}{T_c}\frac{d^2h_c^2}{dt^2}. \quad (7)$$

$H_c(T)$ is given by Eq. (2) and $h_c(t)$ by

$$h_c(t) = H_c/H_0 = 1 - at^2 + bt^3, \quad (8)$$

where

$$a = (A/H_0)T_c^2, \quad b = (B/H_0)T_c^3.$$

Consequently

$$\gamma/V_m = (H_0/T_c)^2(a/2\pi), \quad (9)$$

an expression given previously by Sommerfeld[22] (and by Daunt, Horseman, and Mendelssohn[23] for the special case of a parabolic field relation).

The similarity feature of the critical field curves implies that both H_0/T_c and a are independent of atomic mass, and to the extent that this is quantitatively current, it follows from (9) that γ/V_m is also independent of mass. H_0/T_c is constant to about one part in 800. An estimate of the variability of a may be obtained by comparing the calculated equation for $\Delta H_c(T)$ with the observed data,[24] and is of the order of 1.5 percent. Hence if no other sources of error are present, γ/V_m may be assumed independent of mass to about 1.5 percent. (There is, however, some further uncertainty in a due to the fact that there is a certain amount of choice in fitting an equation to the empirical critical field data; a will vary somewhat depending on whether the coefficients in the equation are chosen for best fit at low temperatures, or near the critical temperature, or whether the mean square deviation over the entire temperature range is minimized. This is simply

[23] Daunt, Horseman, and Mendelssohn, Phil. Mag. 27, 754 (1939).
[24]
where

$$\Delta H_c(T) = \Delta H_c(0) + mT^2 - nT^3,$$

$$m = H_{02}\frac{a_2}{T_{c2}^2} - H_{01}\frac{a_1}{T_{c1}^2}.$$

If critical field curves are geometrically similar $a_2 = a_1$. If $a_2 \neq a_1$,

$$m_{\text{obs}} - m_{\text{calc}} = (H_{02}/T_{c2}^2)(a_2 - a_1).$$

another way of saying that $(d^2H_c^2/dT^2)$ is determined with less certainty than $H_c(T)$ itself.) If the atomic volume V_m is also independent of mass,[25] then γ itself is the same for all isotopes, a conclusion also given by Lock *et al.*[17]

Using the numerical values $H_0/T_c = 82.1$ oersteds/K°, $V_m = 14.2$ cm³ and $a = 1.223$ in Eq. (9) gives $\gamma = 4.46 \times 10^{-4}$ cal/deg²/mole. The direct calorimetric measurements[26] of Keesom and Van Laer[27] determine γ as $4.0 \pm 0.4 \times 10^{-4}$ cal/deg²/mole, which is good agreement.

As stated above, the critical field data presented here are not adequately represented by a parabola, and hence the specific heat and entropy differences cannot be accurately described in terms of simply linear and cubic terms but must contain other higher terms as well. The entropy difference which follows from (2) and (4a) is

$$S_n - S_s = (V_m/4\pi)(2H_0AT - 3BH_0T^2 - 2A^2T^3 + 5ABT^4 - 3B^2T^5). \quad (10)$$

It is also of interest to examine these data in terms of the Gorter-Casimir two-fluid theory.[21] From this point of view the electron assembly in the superconducting state is considered as a two-phase system, a "crystallized" phase of zero entropy consisting of the superconducting electrons and a "gaseous" phase consisting of normal electrons which have a finite entropy given by the Sommerfeld theory. The entropy of the "gaseous" phase per mole of superconductor is

$$S_{n_{el}} = \gamma T x^\alpha, \quad (11)$$

where x is the fractional concentration of normal electrons at temperature T and α is a constant. The condition that the free energy be a minimum leads to the relations

$$x = (2\beta/\alpha\gamma)^{1/(\alpha-1)}T^{-2/(\alpha-1)} \quad (12)$$

and

$$T_c^2 = (2\beta/\alpha\gamma), \quad (13)$$

where T_c = the transition temperature, and β is the free energy difference per mole between normal and superconducting phases at absolute zero and hence

$$\beta = (H_0^2/8\pi) \cdot V_m.$$

It will be seen that (13) is identical in form to (9) and that $\alpha = 1/2a$.

[25] V_m may be slightly mass dependent because of the anharmonicity of the zero-point vibrations. This, however, should be a very small effect and may be estimated by assuming that a small increase in zero-point energy has the same effect in dilating the lattice as the same addition of thermal energy at a higher temperature. This argument suggests that the effect is only of the order of 0.002 percent per mass unit.
[26] W. H. Keesom and P. H. Van Laer, Leiden Communications 252b (1938).
[27] The uncertainty of ±0.4 is our own estimate based on the spread in their observed data.

If $\alpha = \frac{1}{2}$

$$x^\alpha \sim T^2 \quad (14)$$

$$S_{n_{el}} \sim T^3 \quad (15)$$

and the critical field curve is parabolic. The present data for tin show that the critical field is not parabolic, and that α is 0.409 instead of $\frac{1}{2}$. In general it follows from (11) and (12) that

$$S_{n_{el}} \sim T^{-(\alpha+1)/(\alpha-1)}. \quad (16)$$

Hence from our data $S_{n_{el}} \sim T^{2.4}$.

Daunt[28] has shown that the temperature dependence of the penetration depth can be deduced from the Gorter-Casimir thermodynamical model if the square of the penetration depth is assumed to be inversely proportional to the density of superconducting electrons. It follows that

$$(\lambda_0/\lambda)^2 = 1 - t^{-2/(\alpha-1)}, \quad (17)$$

where λ_0 = penetration depth at 0°K, and λ = penetration depth at reduced temperature t. When $\alpha = \frac{1}{2}$ the familiar[29] fourth power law is obtained for the temperature variation of the penetration depth. For $\alpha = 0.409$, the result indicated by the present data for tin, the temperature variation would follow a 3.4-power law, with an uncertainty of perhaps 5 percent in the exponent. Whether or not this divergence from the fourth power is significant is hard to say, since on the one hand the penetration depth measurements are probably not precise enough to exclude the possibility of a 3.4 power, and on the other hand the model from which (17) is derived may be only a crude approximation to the truth.

Finally, it should be remarked that if an equation of the form of (17) does hold, then the temperature dependence of the penetration depth is independent of isotopic mass.

[28] J. G. Daunt, Phys. Rev. 72, 89 (1947). Phys. Rev. 74, 985 (1948).
[29] Daunt, Miller, Pippard, and Shoenberg, Phys. Rev. 74, 842 (1948); also J. M. Lock, Proc. Roy. Soc. (London) A208, 391 (1951).