Critical Field Measurements on Superconducting Lead Isotopes*

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The measurement of the isotope effect upon the superconducting critical field of lead has been extended from T_c to 1.28°K, and an accurate critical-field curve for lead is reported for this temperature range. The measured critical-field curve is expanded as a function of T^2 and used in calculating the thermodynamic properties of lead. The values for the coefficient of the electronic specific heat in the normal state and for the latent heat of the superconducting transition are in good agreement with calorimetric measurements. The electronic specific heat in the superconducting state does not show an exponential $1/T$ dependence but instead a close resemblance to a T^4 dependence below 5°K.

The temperature dependence of the critical field of lead, like that of most superconductors, is not parabolic. However, the observed H_c values lie above a parabola passing through H_0 and T_c which is in the opposite direction from the deviations shown by all other superconductors for which precise data are available. It is shown that an empirical correlation exists for superconductors between the deviation from parabolic behavior and T_c/θ_0, where θ_0 is the Debye temperature at $T=0$°K.

Measurements of the isotope effect upon the critical field below T_c show small differences in the coefficient of the normal electronic specific heat, γ, between specimens but in general give support to the principle of similarity in lead to about the same precision as has been reported for other superconductors.

1. INTRODUCTION

THE results of measurements of the isotope effect in superconducting lead near T_c were reported in a previous article[1] (hereafter referred to as I) with the conclusion that the critical temperature of lead is dependent upon the average isotopic mass and is in good agreement with the equation $T_cM^{\frac{1}{2}}=$ const as are the results from all other superconductors which have been measured.[2] In addition to measurements in the vicinity of T_c, a preliminary study of the isotope effect as a function of temperature was made to test the validity of the similarity principle. The results at temperatures well below T_c were rather unexpected since they showed a large apparent deviation from similarity. The critical field curves for three Pb specimens of different average isotopic mass were observed to separate rapidly as the temperature was lowered below T_c.

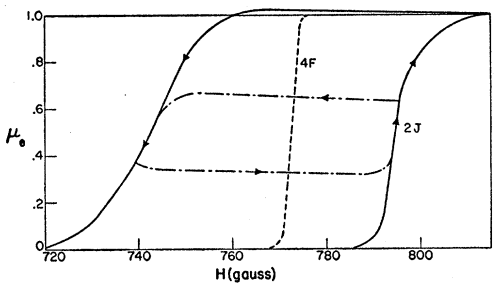

FIG. 1. Example of a magnetic transition in pure Pb specimen $2J$, showing a large hysteresis effect. The nearly vertical dashed line near the center of the loop shows the transition at the same temperature (1.40°K) for specimen $4F$ which showed little hysteresis.

The work to be described here is essentially a continuation of the investigation whose initial phases were described in I. Some progress has been made toward a resolution of the anomalies which beset the low-temperature measurements in I and a rather precise determination of the critical field curve for Pb has now been obtained. Data are presented which permit at least a preliminary assessment of the validity of the similarity principle for the isotope effect in Pb.

2. EXPERIMENTAL

Apparatus and Measuring Method

The cryostat employed throughout this experiment is essentially the same apparatus described by Hake and Mapother.[3] Modifications to this cryostat as well as a discussion of the solenoids which produced the magnetic fields, and the techniques of temperature measurement and control have been given in I. The measurement consists of an isothermal ballistic induction method described in detail in a paper by Cochran, Mapother, and Mould,[4] to which the reader may refer for most of the experimental details.

For any specimen of finite dimensions there is a finite interval of applied field within which the permeability change associated with the superconducting transition occurs. When measuring small shifts in H_c, it is necessary to adopt some criterion for fixing H_c within this interval. Although the basic method used in the present work has been discussed,[4] a special complication arises in the application of this method to Pb. For reasons which are only partially understood at present, Pb

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[1] Hake, Mapother, and Decker, Phys. Rev. **112**, 1522 (1958).

[2] E. Maxwell, Phys. Today **5**, 14 (1952). Also B. Serin, *Progress in Low-Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1955) Vol. I, p. 142.

[3] R. R. Hake and D. E. Mapother, J. Phys. Chem. Solids **1**, 199 (1956).

[4] Cochran, Mapother, and Mould, Phys. Rev. **103**, 1657 (1956).

TABLE I. Properties of measured Pb specimens.[a]

Specimen	$\bar{M}$	L/d	n
138	207.811±0.067	13.3	0.0130
4F	207.271±0.002	22.8	0.0054
702	206.884±0.011	12.4	0.0146

[a] n is the demagnetizing factor for the specimen if it were an ellipsoid with the given length-to-diameter ratio, L/d. $\bar{M}$ is the average isotopic mass.

specimens frequently exhibit a distinctive type of irreversibility which manifests itself as a magnetic hysteresis when transitions are measured by the present method. Since an investigation into the nature and causes of this hysteresis is currently in progress, we shall comment only upon the symptoms and their effects on the present measurements.

A transition showing a pronounced hysteresis effect is pictured in Fig. 1. The distinguishing features are as follows:

(a) The S-N (superconducting-normal) transition is usually broader than the ideal width determined from the specimen dimensions and the upper end of the transition bends over into an extended tail.[5]

(b) The N-S transition is also broad and displaced well below the S-N transition. This type of N-S transition is readily distinguished (by the gradual change in μ_e) from a supercooled N-S transition which also occurs below H_c (but which is quite abrupt).

(c) A hysteresis loop may be traced by cycling the magnetic field when the specimen is in the intermediate state.

(d) The S-N and N-S transitions are approximately equidistant above and below the reversible transition for a good Pb specimen measured at the same temperature. This observation suggests a means of correcting results of measurements on specimens showing hysteresis so as to agree with measurements on more ideal specimens.

This hysteresis effect has a very pronounced temperature dependence, the breadth of the hysteresis loop increasing rather rapidly as the temperature is reduced. This effect is the cause of the large apparent deviations from the similarity principle that were described in I since H_c was determined from S-N transitions. The hysteresis always disappears as the measuring temperature approaches T_c and thus it did not affect measurements near T_c.

Most of the hysteresis can be removed (from most specimens) by annealing at 260°C. Although some of the AEC specimens have retained their hysteretic behavior even after the above annealing treatment, all of the pure natural Pb specimens respond to this treatment. No specimen has been prepared which is entirely free of hysteresis at the lowest temperatures of measurement, but the magnitude of the effect is greatly reduced. Figure 2 shows a small hysteresis loop in the best Pb specimen, 4F, which was entirely free of hysteresis above 3.8°K. It is to be noted that the hysteresis loop is observable only when the field is reduced with the specimen in the intermediate state. If the specimen makes a complete transition into the normal state, subsequent reduction of the applied field results in a supercooled transition which completely obscures the small hysteresis.[6] The way in which we have corrected for this small residual hysteresis as illustrated in Fig. 2. The justification for this correction is largely intuitive and rests on the symmetrical disposition of the S-N and N-S transitions about H_c which is observed in cases where the hysteresis is large. Fortunately the annealing treatment generally eliminates the hysteresis except at the highest values of H_c but here the magnitude of this correction exceeds the magnitude of the isotope shift.

Specimens

The specimens used in this work along with their isotopic mass analyses have been described in I. This same article discusses the chemical purity and preparation of the individual specimens. There is little to be added except that a spectrographic analysis by the Detroit Testing Laboratories of sections from some of the "natural" lead specimens (e.g., specimen 4F) found less than 0.002% impurities. The isotope specimens, on loan from the Oak Ridge National Laboratory, may contain as much as 0.2 to 0.5% impurities but no accurate determination has been attempted to date. Some pertinent properties of the specimens included in the present discussion are listed in Table I.

Specimens were annealed in vacuum at a temperature of 260°C for 8 hours or more to eliminate hysteresis

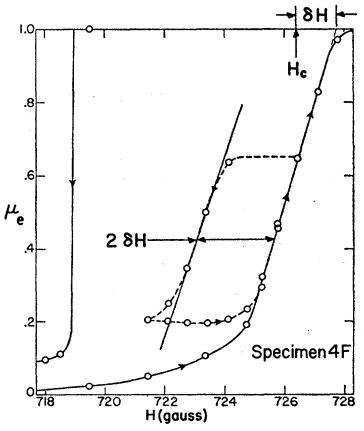

FIG. 2. Small hysteresis loop for a nearly ideal Pb specimen which also shows supercooling when taken completely normal. Temperature of measurement is 2.34°K. δH gives the magnitude of the hysteresis correction. Note the greatly expanded abscissa in comparison with Fig. 1.

[5] Although readily detectable, this is often a rather small effect amounting to a width of 2 or 3 times that expected on the basis of specimen geometry. By usual standards the transition may look quite sharp.

[6] As is apparent in Fig. 2, an S-N-S cycle which includes a supercooled transition also constitutes a type of hysteretic cycle. However, to avoid confusion in the present article we shall reserve the term, hysteresis, to describe permeability cycles in which the N-S transition does not show supercooling.

effects. It is interesting to remark that specimen 138 showed substantial hysteresis after annealing for 21 hours at 200°C. However, the annealing at 260°C reduced the hysteresis to about as low a level as that shown by any other specimen.

3. CRITICAL FIELD CURVE FOR SUPERCONDUCTING LEAD

Experimental Results and Analysis

Three different critical field determinations were made in the course of this work. The results of the first run were reported in the *Proceedings of the Fifth International Low-Temperature Conference*.[7] Unfortunately these measurements were made before the nature of the hysteresis effects in the transition of lead was discovered. After investigation of the hysteresis effects, a second determination was made in the helium region using a simplified cryostat. The precision of temperature measurement on the second run was not as good as can be achieved with the more complex vacuum-jacketed cryostat[1] and so a third determination was made using the latter apparatus. The results discussed in this section were obtained on the third run.

All measurements were made after the temperature had been stabilized for at least 15 minutes. Several readings were taken over a period of one to two hours before changing the temperature to another point. Measurements were made at 39 different temperature points between 1.28°K and 7.17°K. The order of the measured points was taken at random to eliminate systematic errors during the eight days of the run. Temperatures below the boiling point of helium were determined by measuring the helium vapor pressure while a carbon resistor served as a thermometer above this temperature. This resistor must be calibrated against the vapor pressure readings in the helium region and the calibration extrapolated into the region above 4.4°K.

(a) *Temperature Calibration of the Carbon Resistor*

The carbon resistor was calibrated against the vapor pressure of liquid He using the T_{55E} scale.[8] Standard manometric procedures were employed with corrections applied for thermal expansion of the mercury manometer, local gravitational constant, and hydrostatic head of liquid He.

The two-parameter equation, first used by Clement,[9] fits the carbon resistance data to within about 0.005°K in the helium region. However, the deviations of the measured points from this empirical equation are not random and suggest the introduction of another term with a third arbitrary parameter.

In order to extrapolate the carbon resistance calibration above the helium region, several simultaneous measurements of the carbon resistance *vs* H_c were made, where $1.9<H_c<40$ gauss. From these data the value of the carbon resistance at T_c, i.e., $H_c=0$, was determined. Combining this with the recent precise value of T_c for lead[10] provides one more known set of R and T.

Several three-constant equations relating R and T were tried. They were forced to pass through the correct resistance at T_c by weighting this point. The equation which could be most readily forced to fit the data at T_c and at the same time accurately fit the data below 4.4°K was chosen. This equation is of the form

$$\left(\frac{\log R}{T}\right)^{\frac{1}{2}}=a\log R+b+c\left(\frac{T}{\log R}\right)^{\frac{1}{2}}. \tag{1a}$$

Solving for T gives

$$T=\frac{A\log R}{(\log R-B)^3-C}+\frac{\epsilon T^2}{\log R(\log R-B)^2-C}, \tag{1b}$$

where ϵ is very small. Thus T is calculated from the first term and then substituted into the second to give a small correction. The rms deviation for the measured points in the helium region was ± 0.0014°K with $A=2.50983$, $B=1.614587$, $C=0.049401$, and $\epsilon=0.000243$. The calculated temperature was 0.014°K low at T_c; thus an additional correction was made by drawing a smooth curve between the calibration in the helium region and T_c on a difference plot.

After analyzing the critical-field data, a discontinuity appeared between the points measured with liquid helium in the inner can and those measured above the helium region. The high-temperature portion of the curve was about 0.40 gauss above the low-temperature portion in the region of overlap. This discrepancy is thought to be due to the difference in thermal contact between the carbon resistor and its surroundings under the conditions of regulation prevailing above and below the normal boiling point. A difference of 0.4 gauss in H_c corresponds to a difference of 0.003°K in temperature at 4.2°K. Thus a final correction was made to the temperature extrapolation above 4.4°K by not joining it smoothly to the lower temperature calibration but rather by forcing it 0.003°K below the low-temperature calibration at the boiling point of helium.

(b) *Critical-Field Values for Lead*

The accuracy of the H_c values is determined by the precision of the solenoid calibrations. These calibrations were made by nuclear resonance techniques accurate to

[7] Decker, Mapother, and Shaw, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August, 1957* (University of Wisconsin Press, Madison, 1958).

[8] Clement, Logan, and Gaffney, Phys. Rev. **100**, 743 (1955). See note added in proof.

[9] Corak, Garfunkel, Satterthwaite, and Wexler, Phys. Rev. **98**, 1699 (1955).

[10] W. B. Pearson and I. M. Templeton, Phys. Rev. **109**, 1094 (1958).

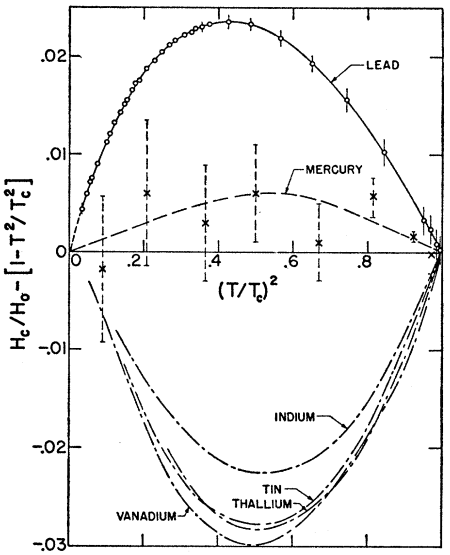

FIG. 3. Comparison of the deviations from the parabolic law for several superconductors.

$\pm 0.015\%$. Errors due to inhomogeneity in magnetic field were reduced to less than $\pm 0.002\%$ by averaging the measured magnetic field over the volume occupied by the specimen. Other small corrections were applied to correct for the residual component of the earth's magnetic field (largely canceled by a Helmholtz pair), the interference in field due to adjacent specimens (see discussion of FIE in I), and to compensate for small drifts in the solenoid current.

The remaining uncertainty is in the determination of H_c from graphs of μ_e *vs* H. In the absence of hysteresis this can be done to a precision of about ± 0.02 gauss, but additional inaccuracies attend the hysteresis correction so that at the lowest temperatures the precision in H_c is probably no better than ± 0.25 gauss.

(c) *Critical-Field Curve for Lead*

Table II summarizes the corrected data and gives our estimate of the errors of measurement. The critical field of lead plotted against T^2 shows a deviation from a parabolic dependence which is shown in Fig. 3 together with the measurements of the nonparabolic shapes of the critical field curves for several other superconductors. The data for mercury in Fig. 3 are taken from Maxwell and Lutes' measurements on a free rod of mercury.[11] We have extrapolated those results to $H_0=408.8$ gauss which is 1.9 gauss below the mean value reported by the authors (410.7 ± 4.0 gauss). This causes the critical field curve for mercury to show a slight deviation from a parabolic shape in the same sense as lead. The uncertainty in the mercury measurement is probably too great to distinguish between this

[11] E. Maxwell and O. S. Lutes, Phys. Rev. **95**, 333 (1954).

TABLE II. Critical-field data for lead specimen 4*F*.

T (°K)	H_c (gauss)[a] corrected	Hysteresis correction[b] (gauss)	Weight
4.2456±0.0015	540.17±0.12	···	0.07
5.4008±0.0036	365.58±0.03	···	0.07
6.5823±0.0056	135.66±0.05	···	0.02
4.6853±0.0028	479.37±0.03	···	0.1
5.7859±0.0046	296.35±0.06	···	0.03
7.0038±0.0054	40.79±0.07	···	0.02
7.1257±0.0052	12.00±0.05	···	0.01
7.1688±0.0053	1.94±0.02	···	0.01
4.9987±0.0029	431.85±0.04	···	0.01
6.1878±0.0056	218.45±0.04	···	0.01
7.0643±0.0053	26.83±0.05	···	0.02
3.8156±0.0009	593.05±0.03	0.04	1
3.5642±0.0010	620.96±0.04	0.08	0.7
3.0140±0.0007	674.81±0.06	0.31	0.8
2.7307±0.0016	698.48±0.09	0.66	0.6
4.3996±0.0015	519.58±0.01	···	0.4
4.1167±0.0014	556.56±0.01	0.01	0.4
3.2671±0.0006	651.28±0.06	0.19	1
2.4905±0.0006	716.48±0.09	1.03	0.7
1.7643±0.0006	760.03±0.15	2.08	0.6
3.9889±0.0009	572.39±0.02	0.02	0.8
3.4268±0.0017	635.27±0.04	0.13	0.3
3.0934±0.0013	667.47±0.09	0.28	0.4
2.2528±0.0008	732.48±0.10	1.40	0.8
1.9486±0.0007	750.59±0.15	1.83	0.3
1.5110±0.0014	771.71±0.20	2.36	0.3
3.7211±0.0007	603.75±0.04	0.06	0.7
2.9350±0.0005	681.58±0.09	0.41	0.6
2.7888±0.0005	693.71±0.07	0.60	0.7
2.6555±0.0007	704.11±0.11	0.74	0.3
2.3452±0.0011	726.51±0.08	1.26	0.5
1.7088±0.0007	762.75±0.18	2.14	0.4
4.1609±0.0008	551.08±0.04	0.01	0.4
1.2840±0.0023	780.33±0.25	2.52	0.2

[a] The error in H_c is the rms error, but does not include the over-all uncertainty in field calibration (about +0.02%) which does not lead to random error.
[b] This is the amount subtracted from the measured H_c to get the corrected H_c.

analysis or that of Maxwell and Lutes; however, this analysis appears to be slightly more consistent with the data. The uncertainties in the magnetic measurements on the other superconductors are about half that for mercury. These superconductors definitely show a deviation from the parabola in the opposite sense to that of lead.

An analytic expression for the critical-field curve for lead was obtained by expanding H_c as a power series in T. The points were given the weights indicated in Table II. This weighting was determined from the over-all uncertainties in T and H_c and the number of measurements at each point. An equation of the form

$$H_c=H_0+\sum_{n=2}^{N} a_n T^n \qquad (2)$$

does not give a very satisfactory fit to the data for $N=3$, 4, or 5. In each of these expansions a_3 is negative, which corresponds to a negative electronic specific heat in the superconducting state for small enough T as shown in the Appendix. For this reason a T^3 term in the expansion of H_c is not acceptable. An expansion in

even powers of T,

$$H_c=H_0+\sum_{n=1}^{N} a_{2n}T^{2n}, \tag{3}$$

does not have this objection provided $a_4>-a_2^2/2H_0$. A least-squares fit to the data was made using a digital computor to determine the coefficients, a_{2n}, for $N=2$, 3, 4, and 5. The coefficients in these expansions diminish very rapidly. The differences between the measured points and the empirical equations for $N=2$, 3, and 4 show definite systematic deviations (see Fig. 4). However, the expansion for $N=5$ gives a very good fit to the data and the measured and calculated differences are reduced to random deviations within the accuracy of the experiment (see Fig. 5).

The final analytical expression is

$$H_c=802.53-13.3484T^2-0.097131T^4+0.00217588T^6 -0.0000319967T^8+0.000000194527T^{10}. \tag{4}$$

The number of significant figures retained in the coefficients of (4) is that necessary to calculate H_c to within ±0.01 gauss. The equation fits the experimental data with a maximum deviation of 0.16 gauss and an rms deviation of ±0.08 gauss which is the order of magnitude of the experimental precision. From this equation $H_0=802.53$ gauss and $T_c=7.1766$°K.

The measured values of H_c^2 were also expanded in a power series of T^2. This expansion gives

$$H_c^2=644184-21500.3T^2+35.8574T^4+5.05647T^6 -0.0658047T^8+0.000387239T^{10}. \tag{5}$$

From this equation $H_0=802.61$ gauss, in good agreement with (4).

From all the methods of analyzing the data, including three other expansions which give a good fit to the data well within the accuracy of the experiment, we give the following values for the constants of the superconducting critical field curve of lead. The error limits stated include the errors from all known sources.

$$H_0=802.6\pm0.4 \text{ gauss},$$
$$(dH_c/dT)_{T=T_c}=-238.4\pm1.2 \text{ gauss/°K}, \tag{6}$$
$$T_c=7.175\pm0.005\text{°K}.$$

This experiment does not determine T_c since the value measured by Pearson and Templeton[10] was entered into the temperature calibration as a known quantity. [The error limits on T_c in (6) are also theirs.]

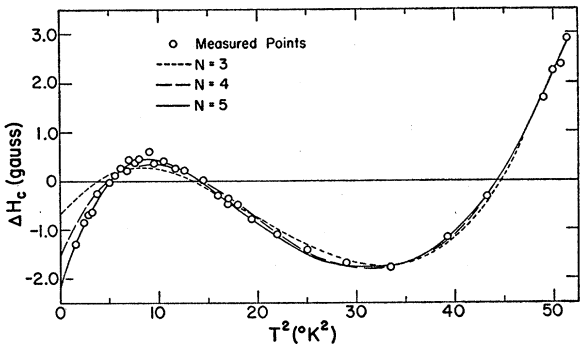

FIG. 4. Deviations of experimentally observed critical field values from the least-squares fit to the expression $H_c=H_0-AT^2+BT^4$. Experimental points are indicated by the circles. The effect of adding higher powers of T^2 to the expansion for H_c is shown by the three curves. Each curve gives the deviation for a least-squares fit to a series expansion terminated at T^{2N}.

(d) *Thermodynamic Analysis*

From a Clausius-Clapyron type argument based on the critical field curve of a superconductor it may be shown[12] that

$$\Delta S=S_n-S_s=\frac{-VT}{8\pi}\frac{d(H_c^2)}{dT}, \tag{7}$$

$$L=T\Delta S=\frac{-VT}{8\pi}\frac{d(H_c^2)}{dT}, \tag{8}$$

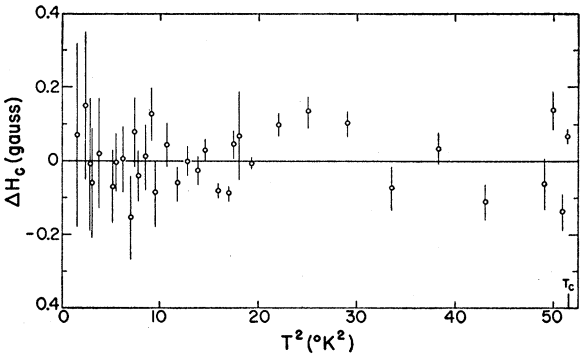

FIG. 5. Deviations of observed H_c values for Pb from Eq. (4). The error limits do not include the uncertainty in the absolute temperature in the region above the boiling point of liquid helium

and

$$\Delta C=C_n-C_s=\frac{-VT}{8\pi}\frac{d^2(H_c^2)}{dT^2}, \tag{9}$$

where the subscripts, s and n, denote the superconducting and normal states; S, the molar entropy; L, the latent heat of the transition; C, the molar specific heat; and V, the molar volume.

It is usually assumed (with some theoretical justification[13]) that the total specific heat may be expressed as the sum of a lattice contribution and an electronic contribution, and, further, that the lattice contribution is the same in both the superconducting and normal states. Accordingly ΔC may be regarded as the difference between the electronic contributions to the specific heat in the superconducting and normal states. Denot-

[12] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952), Chap. III.

[13] G. V. Chester, Phys. Rev. **104**, 883 (1956).

ing these contributions by C_{es} and C_{en}, we have

$$\Delta C = C_{en} - C_{es} = \gamma T - C_{es}(T) \qquad (10)$$

upon inserting the Sommerfeld result, $C_{en} = \gamma T$.

It was originally noted by Daunt and Mendelssohn[14] that the expression for ΔC will be dominated by γT at sufficiently low temperatures if the C_{es} variation with temperature is more rapid than a linear dependence. On the basis of experimental work it appears that the latter requirement is amply fulfilled, and it is thus possible to determine γ from the limiting value of $d^2(H_c^2)/dT^2$ at low values of the reduced temperature, $t = T/T_c$, using Eq. (9). Having determined γ, $C_{es}(T)$ may be derived from Eq. (10). Considering all possible methods of analysis from the several expansions of the

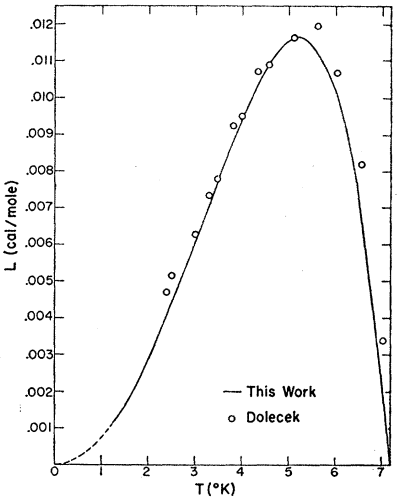

FIG. 6. Latent heat of the superconducting transition in Pb. Circles show the values reported in reference 17.

data and all sources of error, this experiment yields[15]

$$\gamma = 3.06 \pm 0.04 \text{ millijoules/mole-deg}^2,$$
$$\Delta C(T_c) = 0.0581 \pm 0.0007 \text{ joule/mole-deg}. \qquad (11)$$

The value of γ for lead calculated from the low-temperature magnetic data of Daunt and Mendelssohn[14] is 2.95 millijoules/mole-deg^2. Calorimetric measurements by Horowitz *et al.*[16] yielded $\gamma = 3.13$ millijoules/mole-deg^2 and the value of γ reported by Dolecek[17] in connection with measurements of the latent heat of the superconducting transition is 3.3 millijoules/mole-deg^2. All of these values are in good agreement with (11)

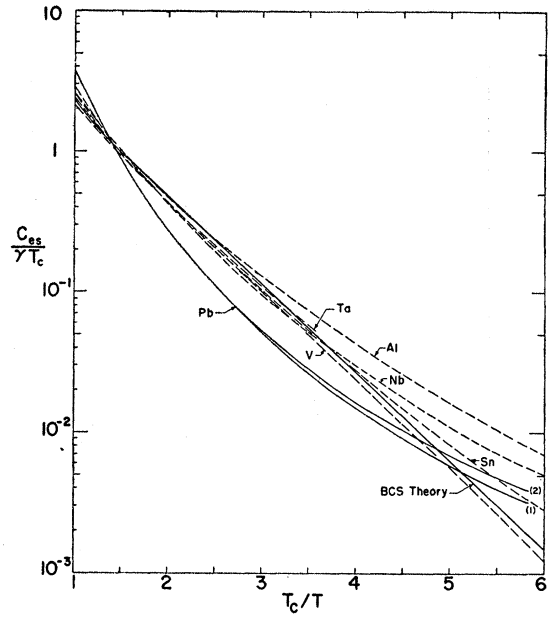

FIG. 7. Electronic specific heat in the superconducting state (C_{es}) for several superconductors. The two curves for Pb marked (1) and (2) were calculated from Eqs. (4) and (5), respectively.

in that the γ determined in this work lies well within the error limits of these previous determinations.

The discontinuity in the specific heat at T_c has been measured calorimetrically by Clement and Quinnell.[18] They reported a value of 0.053 ± 0.002 joule/mole deg which is considerably lower than the value in (11) calculated from this experiment.

Calculation of the latent heat by Eq. (11) yields nearly identical values for both expansions (4) and (5) at all temperatures above 1.2°K. These results are shown in Fig. 6 along with Dolecek's latent heat data.[17] Our results agree rather well with Dolecek's measurements between 3 and 5°K but there is some disagreement both above and below this temperature region.

The superconducting electronic specific heat calculated from Eqs. (4) and (5) is plotted as Pb(2) and Pb(1) on a semilogarithmic graph of $C_{es}/\gamma T_c$ *versus* T_c/T in Fig. 7. Below 2.4°K ($T_c/T > 3$) the two expansions give different values for $C_{es}(T)$. Two causes contributing to this difference are (a) the small magnitude of C_{es} in comparison with γT at these temperatures, and (b) the fact that the experimental data do not extend below 1.28°K, thus making the derivatives of the expansions for H_c less reliable at lower temperatures. Instead of using an empirical expansion of the data to calculate the derivatives of H_c, it is possible to find $\Delta H_c/\Delta T$ by point-to-point differences. This method also gives some idea of the scatter in the data. Calculating ΔS in this manner (for $T < 2.5$°K) and subtracting it from γT gives an idea of the accuracy in determining γ (i.e., for a value of γ which is too small,

[14] J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. (London) **A160**, 127 (1937), also Daunt, Horseman, and Mendelssohn, Phil. Mag. **27**, 754 (1939).

[15] The value $V = 17.86$ cc/mole for Pb was used in the calculation. This value was obtained by making an approximate correction to the room temperature molar volume to account for thermal expansion.

[16] Horowitz, Silvidi, Malaker, and Daunt, Phys. Rev. **88**, 1182 (1952).

[17] R. L. Dolecek, Phys. Rev. **94**, 540 (1954).

[18] J. R. Clement and E. H. Quinnell, Phys. Rev. **85**, 502 (1951).

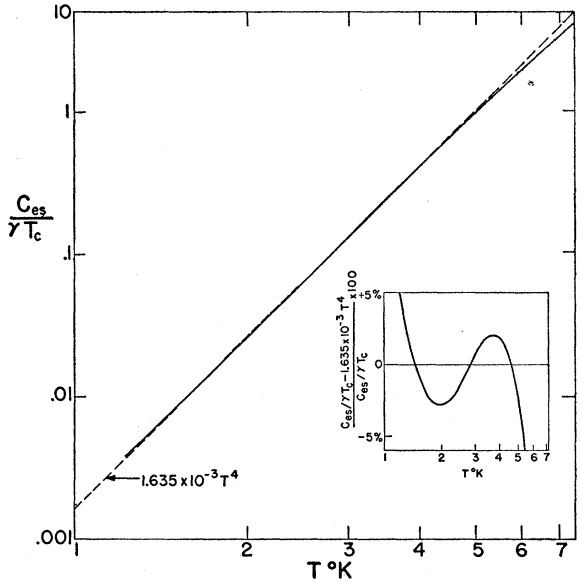

FIG. 8. Comparison between the function $1.635\times10^{-3}T^4$ and $C_{es}/\gamma T_c$ values deduced from the critical-field curve of Pb. Inset shows the deviation from a T^4 law.

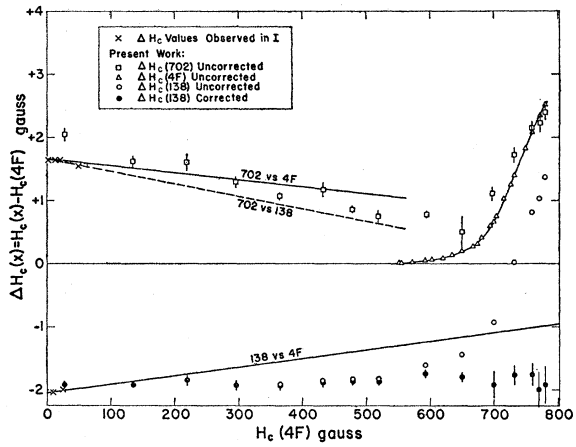

FIG. 9. Critical-field differences between Pb specimens of different isotopic mass. The reference line, $\Delta H_c=0$, corresponds to the corrected critical field of specimen $4F$ [i.e., the critical field represented by Eq. (4)]. The slanting lines show the differences expected on the basis of the similarity principle. Values of ΔH_c near T_c obtained in I are shown by crosses.

$S_{es}=\gamma T-\Delta S$ goes negative at the lower temperatures, and if a large value is picked, S_{es} becomes linear with temperature). The limits on γ thus imposed are in agreement with (11). Since γT is so much larger than C_{es} in this low-temperature region, the scatter in the data suggest an uncertainty in the quantity $C_{es}(T)$ of about 50% at 2.5°K and 400% at 1.2°K. The most recent calorimetric measurements on other superconductors are also plotted in Fig. 7 as well as the theoretical curve from the calculations of Bardeen, Cooper, and Schrieffer.[19]

A plot of $\log(C_{es}/\gamma T_c)$ *versus* $\log T$ shows a remarkable resemblence to the function $C_{es}/\gamma T_c=1.635\times10^{-3}T^4$ for $T<5$°K. The comparison between $1.635\times10^{-3}T^4$ and $C_{es}/\gamma T_c$ for lead is given in Fig. 8.

4. PRINCIPLE OF SIMILARITY

Because of the complications of hysteresis (which could not be removed in some specimens) our best measurements were made using only specimens 702, 138, and $4F$. In considering the experimental validity of the similarity principle, only the most reliable observations will be mentioned.

Isotope Effect on the Critical Field of Lead

Critical-field differences were determined by alternately measuring the critical fields of one of the isotope specimens and the standard specimen, $4F$, in rapid succession. After determining H_c for each transition, critical-field differences were calculated by comparing each H_c with the average of the preceding and following value of H_c for the standard specimen.

At the time of these measurements it was thought that a transition was reversible if it was near ideal sharpness and showed supercooling. All of the transitions from which the present results are obtained satisfied these conditions (except for specimen 702 near T_c). However, as discussed above, a hysteresis narrower than the amount of supercooling can only be detected by measuring the extent of reversibility of the flux changes in the intermediate state, and thus the criteria of sharpness and supercooling are insufficient to establish reversibility. Measurements of the hysteresis in the intermediate state were made for specimens 138 and $4F$ in the final run and an approximate correction was possible in the case of these specimens. The values of ΔH_c as measured and after being corrected for hysteresis are plotted in Fig. 9. The ordinate in Fig. 9 gives the difference between the H_c value of a particular specimen and the *corrected* H_c value of the standard specimen. Thus the points shown in Fig. 9 for specimen $4F$ give the magnitude of the hysteresis correction which was applied to the H_c data in deriving the critical-field curve described in the previous section. All of the specimens showed some hysteresis as evidenced by the rapid rise in the uncorrected ΔH_c points as H_0 is approached. The measured values for specimen 702 could not be corrected for hysteresis since the necessary intermediate-state measurements were not made for this specimen. After making the hysteresis correction the points for specimen 138 follow a reasonably straight line, indicating a shift independent of temperature. Similar behavior has been reported in earlier measurements on Pb isotopes.[20]

The data described in I are shown in Fig. 9 by the crosses near $H_c=0$. The earlier data were in excellent agreement with the expected isotope effect, $M^{\frac{1}{2}}T_c$

[19] Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175 (1957).

[20] Serin, Reynolds, and Lohman, Phys. Rev. **86**, 162 (1952).

$=$const. Although the points for specimen 138 agree well, the points for 702 are about 0.4 gauss higher than the earlier measurements. It seems probable that this difference is due to a broadening (by a factor of about 2) in the 702 transition which was observed in the last run in measurements near T_c. The width of the 702 transitions in I was very close to the ideal value of nH_c and thus those measurements are considered more reliable at this temperature. No explanation can be offered for this change in the behavior of a specimen with time, but the implication is clear that subtle agencies remain which have yet to succumb to our experimental control.

Principle of Similarity

The solid lines in Fig. 9 show the differences in H_c to be expected between specimens on the basis of the similarity principle.[21] In preparing Fig. 9, specimen 4*F* was chosen as the standard of comparison since from the standpoint of chemical purity as well as magnetic behavior it was the best specimen. However, it is possible to examine the validity of similarity for any two specimens and, indeed, the H_c differences between specimens 138 and 702 are possibly nearer to similarity than their respective differences from specimen 4*F*. The dashed line shows where the results of $\Delta H_c(702)$ should lie if similarity held between the critical field curves of specimens 138 and 702.

The magnitude of $\Delta H_c(138)$ is consistently larger than that predicted by the similarity principle. The difference between $H_0(138)$ and $H_0(4F)$ is about 1.7 times as large as one would expect for an $M^{\frac{1}{2}}$ dependence. At the larger values of H_c, where the hysteresis correction is of the same order of magnitude as ΔH_c itself, such a discrepancy is not too conclusive, but, in the range $0<H_c<550$ gauss where $\Delta H_c(138)$ is rather accurately known, there is definite evidence that the critical field curves of 138 and 4*F* are nonsimilar. (However, as discussed below, there is still doubt that this is solely due to the isotopic mass.) The uncorrected points for specimen 702 lie between the results expected on the basis of similarity between 702 *vs* 138 and 702 *vs* 4*F* and, for the reasons mentioned previously, the experimental uncertainty is somewhat greater.

Sources of Error

The estimated over-all uncertainty of each ΔH_c is represented by the vertical lines through the points in Fig. 9. Corrections for inhomogeneity in the magnetic field and the field interference between specimens amount to as much as 8% of ΔH_c. However, these corrections can be determined accurately and do not increase the measured uncertainty in ΔH_c more than 1%. The largest and most uncertain correction is that for irreversible transitions which, because of the small amount of data available to determine the hysteresis width, is believed to be accurate only to within about 15% of ΔH_c at the lowest temperatures.

Another factor which may influence the results on similarity is that of specimen purity. Lynton, Serin, and Zucker[22] have measured the effects of impurities in tin on γ. For tin, a change of 0.2% in γ corresponds to an impurity concentration between 0.03 and 0.2% depending upon the nature of the impurity. In earlier work Serin, Reynolds, and Lohman[20] reported that Pb with 0.2% Sn added showed a 1.2 gauss increase in H_c which was independent of temperature from 4.2 to 1.6°K. Specimen 138 may contain as much as 0.5% impurities while specimen 702 may contain about 0.2%. Thus the departure from similarity observed in Fig. 9 could be due to the impurities in the isotope specimens but it is difficult to reach any convincing conclusions on the basis of present information.

The chemical impurities of the AEC specimens are at least an order of magnitude greater than for specimen 4*F*. Thus a superficial consideration of the data of Fig. 9 might attribute the slightly better "similarity" exhibited by 702 *versus* 138 to the fact that both are specimens from the same source and are displaced relative to the very pure 4*F* specimen by an impurity effect common to both. Unfortunately the chemical purity of the AEC specimens is not known at present. The only data on chemical purity available relates to the condition of the powdered oxide specimens as supplied by the AEC and thus cannot be regarded as representing much more than probable upper limits of impurity in the crystalline specimens on which the measurements were made.

5. CONCLUSIONS

Superconducting Critical Field Curve for Lead

Prior to the present measurements on Pb, most superconductors (for which data of sufficient precision were available) showed a negative deviation from a parabolic temperature dependence (see Fig. 3). A similar behavior for H_c *vs* T has been derived theoretically by Bardeen, Cooper, and Schrieffer.[19] The only exception to this rule was the case of mercury which was reported to be parabolic.[11] The present results are interesting in showing a positive deviation from parabolic behavior of nearly the same magnitude as the negative deviation of tin. A complete theory of superconductivity should account for these differences.

Corak and Satterthwaite[23] have remarked that the "anomalously" parabolic character of the H_c curve for mercury may be related to its relatively low Debye characteristic temperature θ. Extending this suggestion it appears that there is a rather good correlation be-

[21] Lock, Pippard, and Shoenberg, Proc. Cambridge Phil. Soc. **47**, 811 (1951).

[22] Lynton, Serin, and Zucker, J. Phys. Chem. Solids **3**, 165 (1957).

[23] W. S. Corak and C. B. Satterwaite, Phys. Rev. **102**, 662 (1956).

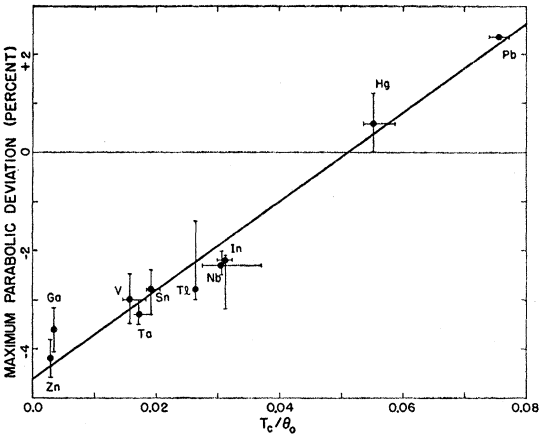

FIG. 10. Empirical correlation among superconductors between T_c/θ_0 and observed deviation from parabolic critical-field curve. The ordinate in this figure gives the maximum amplitude of deviation for each element when plotted as in Fig. 3.

tween the quantity T_c/θ_0 (where θ_0 is the limiting value of Debye temperature as $T \rightarrow 0°K$) and the observed deviation from parabolic temperature dependence. As a measure of deviation from parabolic behavior we have taken the maximum amplitude of deviation between experimental critical field curve and a parabola passing through H_0 and T_c (in reduced coordinates as shown in Fig. 3). The values for several superconductors are plotted in Fig. 10 and a roughly linear relation between deviation and T_c/θ_0 exists. Goodman[24] has recently drawn attention to a qualitatively similar relation between T_c/θ_0 and the quantity $\eta=H_0^2/8\pi\gamma T_c^2$, where γ is the coefficient of the normal electronic specific heat. The quantity η is interpreted as a measure of the limiting value (as $T \rightarrow 0°K$) of the energy gap for the superconducting state.

The thermodynamic calculations based on our critical field data appear to be in irreconcilable disagreement with the two-parameter exponential law of corresponding states, originally suggested on the basis of calorimetric measurements of C_{es} on vanadium and tin.[23,25] More recent calorimetric measurements on other superconducting elements have also shown significant deviations from the old law and there now seems to be general agreement[26] that additional parameters will be necessary for a valid law of corresponding states.

If ΔC is separable as specified by Eq. (10), it can be shown thermodynamically that the form of the temperature dependence of C_{es} is quite sensitive to the form of the parabolic deviation (Fig. 3). As shown by Corak and Satterthwaite,[23] the negative deviations of Sn and V conform with their exponential expressions for C_{es} (except near T_c). (Their law of corresponding states may be regarded as another way of stating the similarity of the parabolic deviations of Sn and V.) It has long been recognized that zero parabolic deviation gives a T^3 dependence of C_{es} and, as shown above, the positive deviation of Pb approximates a T^4 dependence. It can also be shown that the more rapid T dependence persists to lower reduced temperature (T/T_c) as the parabolic deviation becomes more positive.

The accuracy of the present measurements appears sufficient to rule out an exponential C_{es} in the case of Pb for T greater than about $0.3T_c$ if the assumptions implied by the thermodynamic analysis are valid. At lower temperatures C_{es} becomes too small to permit the temperature dependence to be reliably determined. Thus these results do not rule out the ultimate emergence of the exponential dependence of C_{es} upon T at the lowest temperatures which is expected on the basis of the energy gap model.[26]

It is apparent that the reliability of our results rests in considerable measure upon the validity of our criterion for determining H_c for a thermodynamically reversible transition. An experimental verification of reversibility can be accomplished in principle by a comparison of magnetic and calorimetric measurements and within the limitations of accuracy of existing calorimetric data such comparisons are reassuring. However, the significance of such comparisons is weakened by the circumstance that the experimental resolution of the magnetic measurements greatly exceeds the resolution possible in calorimetric techniques. For example, a value of γ calculated from H_c data uncorrected for hysteresis would still be in good agreement with the calorimetric data even though this means a change in H_c many times the precision of the magnetic measurement. In the case of Pb (and other superconductors having low θ values), the achievement of a comparable precision in calorimetric measurements seems unattainable at present since the electronic specific heats constitute such a small fraction of the total specific heat. In the absence of firm procedures for corroborating the reversibility of the magnetically determined H_c (especially at the lowest temperatures), a certain amount of dead reckoning seems unavoidable and, in consequence, the high precision of the magnetic determinations themselves may not be a completely reliable index of the accuracy of the thermodynamic quantities. These reservations apply mainly to data taken at temperatures below the appearance of hysteresis and thus would not significantly alter the character of the critical-field curve.

Principle of Similarity in the Isotope Effect

Taken at face value, the data of Fig. 9 show a deviation from similarity which is greater than the known experimental error. In assessing the significance of such deviations the criterion that $H_0/T_c=\alpha$ be independent of isotopic mass has sometimes been employed. With

[24] B. B. Goodman, Compt. rend. **246**, 3031 (1958).
[25] Corak, Goodman, Satterthwaite, and Wexler, Phys. Rev. **102**, 656 (1956).
[26] Biondi, Forrester, Garfunkel, and Satterthwaite, Revs. Modern Phys. **30**, 1109 (1958). We are indebted to the authors for supplying a copy of this work in advance of publication.

TABLE III. Maximum variation of γ and H_0/T_c for isotopes of superconductors.

Element	$\Delta\gamma_{max}$ percent	$\Delta(H_0/T_c)_{max}$ percent	Source
Sn	0.14	···	Lock, Pippard, and Shoenberg[a]
Hg	0.5	···	Serin, Reynolds, and Nesbitt[b]
Sn	···	0.4	Serin, Reynolds, and Lohman[c]
Sn	1.5	0.12	Maxwell[d]
Pb	0.3	0.10	Present work

[a] See reference 21.
[b] Serin, Reynolds, and Nesbitt, Phys. Rev. **84**, 691 (1951).
[c] See reference 20.
[d] E. Maxwell, Phys. Rev. **86**, 235 (1952).

the small range of mass available in the case of Pb, very little change in α is to be expected and, while it may be said of the present results that α is constant to 1 part in 10^3, this is more a comment on the experimental accuracy than a statement of substantial physical import.

On physical grounds it is to be expected that the similarity principle might fail in the case of Pb owing to a small mass dependence of γ.[27] However, the deviations from similarity observed here, as evidence by the variation of γ, do not support this. Although deviations in γ of about 0.3% exist, a proper correlation with isotopic mass is lacking since both the AEC specimens have lower γ values than the pure natural specimen, $4F$. On the basis of the present evidence we are inclined to attribute the observed deviations to an impurity effect since, as mentioned above, the impurity limits on the AEC specimens are greater than for specimen $4F$. The impurity question represents the major experimental uncertainty of these measurements so far as the similarity principle is concerned.

There have been several measurements of the similarity principle in the isotope effect for different superconductors with most authors concluding that the principle is valid. A comparison of the values obtained for the maximum variation of γ or H_0/T_c is presented in Table III from which it may be seen that despite the small magnitude of the isotope effect in Pb, the present results "verify" the similarity principle with about the same precision as previous work. The experimental results seem unanimous in indicating that no large deviations from similarity occur (although large deviations were hardly to be expected). It seems clear that the present measurements involve enough uncertainty to preclude a rigorous test of the similarity principle, and uncertainties of equal or greater magnitude exist in most of the previous work. Thus it is our opinion that there is enough latitude in the experimental error of work to date to conceal a possibly significant deviation from similarity. Further efforts will be made to improve the preparation of our specimens in the hope of removing some of the present uncertainty.

[27] G. V. Chester (private communication).

ACKNOWLEDGMENTS

We remain indebted to G. DePasquali for continued assistance in the chemical preparation of the Pb isotope specimens and to the Stable Isotopes Division of the Oak Ridge National Laboratory for making the specimens available. The assistance of C. L. Wolff and F. A. Otter in making the measurements is greatly appreciated. The facilities of the University of Illinois Digital Computer Laboratory made possible a much more thorough data analysis than would have been feasible by manual computing techniques. Fellowships from the Celanese Corporation of America and the National Science Foundation provided support for one of us (D.L.D.) during the course of this work.

APPENDIX. ELECTRONIC SPECIFIC HEATS FROM POWER SERIES EXPANSIONS OF $H_c(T)$

We assume that $H_c(T)$ can be expanded in a power series of the form[28]

$$H_c(T)=H_0-a_2T^2+a_3T^3+a_4T^4+\cdots. \quad (1a)$$

Squaring this expression gives

$$H_c^2=H_0^2-2a_2H_0T^2+2a_3H_0T^3+(2a_4H_0+a_2^2)T^4+\cdots.$$

Differentiating H_c^2 with respect to T twice, we get

$$d^2(H_c^2)/dT^2=-4a_2H_0+12a_3H_0T+12(2a_4H_0+a_2^2)T^2+\cdots.$$

ΔC, the difference between the electronic specific heats in the normal and superconducting states, is related to $d^2(H_c^2)/dT^2$ through Eq. (9); therefore

$$(8\pi/V)\Delta C=4a_2H_0T-12a_3H_0T^2-12(2a_4H_0+a_2^2)T^3+\cdots. \quad (2a)$$

But $\Delta C=\gamma T-C_{es}(T)$. Therefore $\gamma=a_2H_0V/2\pi$ and

$$C_{es}(T)=(3a_3H_0V/2\pi)T^2+3(2a_4H_0+a_2^2)(V/2\pi)T^3+\cdots. \quad (3a)$$

Thus if $a_3<0$, then $C_{es}(T)$ will be negative for small enough T.

If the expansion in (1a) is terminated at the T^3 term, then any critical field which deviates above the parabola will have $a_3<0$. As more terms are added to the expansion for lead, a_3 as determined by least squares becomes less and less negative until, for the least-squares expansion terminating with T^6, one has a positive a_3.

Most measured critical-field curves deviate below a parabola. A power series expansion of these curves terminated at the third term will have a positive a_3, but

[28] The term linear in T must be excluded from the expansion (1a) so that ΔS, which by (7) is proportional to $d(H_c^2)/dT$, goes to zero as T approaches zero, as required by the third law of thermodynamics.

this coefficient usually becomes negative if one more term is included in the expansion.[11,29]

If the T^3 term is excluded from the expansion of $H_c(a_3=0)$ then $C_{es}(T)$ will remain positive at the lowest temperatures provided $a_4 > -a_2^2/2H_0$. We conclude that the term in T^3 should not be used in the expansion of $H_c(T)$ and that a more desirable expansion than (1a) is of the form

$$H_c(T)=H_0+\sum_{n=1}^{N} a_{2n}T^{2n}. \tag{4a}$$

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

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Effect of a Magnetic Field on Thermionic Emission from Molybdenum*

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An experiment that was performed to explore the possible effect of an external magnetic field on thermionic emission from a clean metal surface demonstrated that an applied field of 6000 gauss or less has no effect on the saturation current density. The purpose of this study was to resolve, if possible, the disagreement between the work of Shelton and that of Nottingham and Hutson on the energy distribution of thermionically emitted electrons.

I. INTRODUCTION AND BACKGROUND

RECENT studies of thermionic emission from pure monocrystalline metal surfaces suggested the possibility that a magnetic field of a few thousand gauss applied normal to the surface might affect the saturation current density. An earlier study by Nottingham[1] of retarding potential plots on both pure and thoriated tungsten filaments had shown that the distribution of the emitted electrons was non-Maxwellian, and exhibited a marked deficiency in low-energy electrons. Nottingham also found that the observed data were very well approximated if an internal reflection of these slow electrons from the metal surface was assumed. The reflection coefficient was given by

$$R=e^{-V/0.191}.$$

Here V is related to the energy associated with the surface-directed component of momentum p in excess of that required to carry the electron to infinity at zero applied field, as given by $eV=p^2/2m$. The fact that the empirical parameter 0.191 ev, as determined by experiments with thoriated filaments independently of their state of activation and also for tungsten filaments, suggested that the reflection was fundamental in nature.

Hutson[2] found further evidence of this deficiency in an experiment of quite a different nature. He measured the energy distribution of electrons emitted from the various directions of a monocrystalline tungsten wire, by passing them through a 180° magnetic velocity analyzer. He found the distributions to be in close agreement with the Nottingham reflection hypothesis for all directions of the crystal.

A more recent experiment by Shelton[3] failed to show any evidence of this effect. Shelton's work yielded an ideal retarding potential plot on pure tantalum, performed in plane-parallel geometry, and employing single crystals of the metal for both emitter and collector. The plot was a very close approximation to that predicted by a Maxwellian distribution with no reflection.

A distinctive feature of the Shelton experiment was the use of a strong magnetic field (approximately 3000 gauss) directed normal to the surface of the emitter; its purpose was to collimate a narrow beam of electrons which passed between the emitter and collector crystals. The striking difference between the results of Shelton's experiment and of the work of Nottingham and Hutson was considered sufficient reason for investigating the effect of a magnetic field alone.

II. APPARATUS

The simplest means of investigating the effect of a magnetic field would be to employ a broad, thin ribbon filament, so that nearly all of the emitting surface would be normal to the field, and a cylindrical anode that would collect the total saturation current regardless of azimuthal angle. Molybdenum was chosen as the metal for emitting filament. It fulfilled all of the requirements of the experiment, and a supply of thin sheet stock of high purity was available.

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[1] W. B. Nottingham, Phys. Rev. 49, 78 (1936).

[2] A. R. Hutson, Phys. Rev. 98, 889 (1955).

[3] H. Shelton, Phys. Rev. 107, 1553–1557 (1957).