Hamiltonians of the spin system. It is evaluated from

$$\tanh(\gamma Z\xi)\,\{\exp(-2\gamma)+\cosh[2\gamma\{1+(Z-1)^2\xi^2\}^{\frac{1}{2}}]\}=\cos2\theta\,\sinh[2\gamma\{1+(Z-1)^2\xi^2\}^{\frac{1}{2}}], \quad (3)$$

with the help of the relation $\tan2\theta=-1/(Z-1)\xi$ quoted earlier.

Utilizing this result, we can numerically obtain the parallel and perpendicular magnetic susceptibilities, $\chi_{\parallel}$ and $\chi_{\perp}$, below the Curie point from Eqs. (1) and (2), respectively. The results for the case $Z=6$ are plotted in Fig. 1, from which we notice that the perpendicular magnetic susceptibility decreases with decreasing temperature in contrast to other theories, which give very little temperature dependence. This is due to the existence of the anti-Curie point in Nakamura's theory.

The antiferromagnetic susceptibility below the Curie point has been calculated from the usual relation $\chi=(\chi_{\parallel}+2\chi_{\perp})/3$. Figure 2 shows the variation of χ/χ_C with T/T_C, according to both the present theoretical calculations and the experimentally obtained values of Bozorth and Nielsen. The two curves are in good agreement.

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Isotope Effect on the Superconducting Transition in Lead*

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Observations of the difference in critical fields of superconducting Pb specimens of different isotopic mass are described. Measurements are made using the Meissner effect and a ballistic induction method in the range from 7.2 to about 1.4°K. The results near T_c verify the theoretical prediction that $T_c=\text{const}\times M^p$, where M is the average isotopic mass, and yield a value of $p=-0.501\pm0.013$. The measurements at lower temperatures are inconclusive in their implications for the isotope effect, since all specimens measured exhibit large deviations from the predictions of the similarity principle. The deviations are apparently not related to the isotopic mass of the specimens. The agency responsible for the observed deviations has not been isolated, but it is believed that the anomalous H_c values are characteristic of thermodynamically irreversible transitions. Thus the present results are not believed to constitute genuine evidence of a deviation from the similarity principle.

1. INTRODUCTION

THE superconducting isotope effect refers to a displacement of the critical field curve for a superconducting element which is observed when specimens of different isotopic mass are measured. The earliest experiments seeking evidence for such an effect were made using specimens of naturally occurring lead which differed in average isotopic mass by about ½%. The sensitivity achieved in these experiments was insufficient to resolve the very small effect and negative results were reported.[1,2] The isotope effect was first discovered in 1950 for the case of mercury,[3,4] and subsequent work by a number of investigators has confirmed its existence for the elements, tin, thallium, and lead.[5]

The isotope effect is usually described by stating

$$T_c=\text{const}\times M^p, \qquad (1)$$

where T_c is the zero-field critical temperature and M is the average isotopic mass of the superconducting specimen. According to recent atomic theories[6,7] of superconductivity, the exponent p should have the value -0.5, and this expectation has been reasonably well confirmed for all the elements which have been measured with the exception of lead, for which a value -0.73 has been reported.[8,9] In view of this situation it seemed to us that an experimental re-examination of the isotope effect in lead might be desirable.

A brief preliminary account of our first measurements, made just below the critical temperature, has already appeared.[10] This article will cover these measurements in greater detail, and will also report some results obtained in additional measurements which extended from T_c down to about 1.3°K.

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[2] E. Justi, Physik. Z. 42, 325 (1941).

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[5] 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.

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[7] J. Bardeen, Phys. Rev. 80, 567 (1950), and most recently, Bardeen, Cooper, and Schrieffer, Phys. Rev. 108, 1175 (1957).

[8] M. Olsen, Nature 168, 245 (1951).

[9] Serin, Reynolds, and Lohman, Phys. Rev. 86, 162 (1951).

[10] Hake, Mapother, and Decker, Phys. Rev. 104, 549 (1956).

2. EXPERIMENTAL

a. Specimen Preparation

The specimens used in these measurements were prepared from five samples of lead which were obtained on loan from the Stable Isotopes Division of the Oak Ridge National Laboratory. These samples were artificially enriched in certain isotopes and were chosen to give uniform coverage of the available range of average isotopic mass. Specimens were also prepared from a sample of "natural" lead obtained from the American Smelting and Refining Company. An analysis of the Detroit Testing Laboratories of several of the natural lead specimens showed them to be about 99.998% pure. An indication of the chemical purity of the Atomic Energy Commission samples is given in the first column of Table I and is based on a detailed spectroscopic analysis supplied by Oak Ridge. Since the chemical analysis refers to the AEC samples prior to our reduction and crystallization, these purities can be regarded as lower limits which may have been improved in our specimen preparation. Chemical analysis of the actual measured specimens will be done later and any significant deviations from the situation described here will be reported.

The lead samples from Oak Ridge were received in the form of oxides and chromates. The chromates were first converted to lead oxide, and then all samples were reduced by heating in an atmosphere of pure, dry hydrogen. The reduction was carried out in two steps. First, the sample was kept at 315°C for eight hours, and then the temperature was raised to 450°C and maintained for another eight hours, leaving metallic spheres of lead and a small amount of black powder. The lead spheres were separated with tweezers and melted under vacuum in a Pyrex tube. By inclining the tube and shaking gently, the molten lead was caused to flow through two capillary constructions into an Aquadag coated tube and sealed off under vacuum.

The small tube containing the lead was placed in an electric furnace which produced a temperature gradient of about 15 C°/cm over the specimen at the melting temperature of lead. The lead was remelted and then recrystallized by reducing the current to the furnace so that the temperature dropped at the rate of about 20 C°/hr, crystallization occurring from the bottom to the top of the specimen. This procedure did not always produce single crystals, but the specimen always had a very large grain size. After cooling, the glass was etched from the specimen with concentrated hydrofluoric acid and the Aquadag removed by gently rubbing the surface with gauze soaked with alcohol.

Two specimens were formed from the *FQ*-704(*a*) isotope sample and one from each of the other Oak Ridge samples. One natural lead specimen, *G*1, was prepared in the same manner as the isotope specimens, while the other natural specimens, 9*F* and 4*F*, were simply melted in vacuo and crystallized in the gradient furnace without the reduction and purification described above. The masses of the specimens ranged from about 0.6 to 1 gram and all specimens were cast in cylindrical shape with a diameter close to 1.8 mm. Because of the differences in length the effective demagnetizing factors of the specimens varied from 0.015 for specimen 702 to 0.0054 for specimen 9*F*.

The isotopic mass analysis of each specimen is given in Table I. The analyses of the AEC specimens are those furnished by Oak Ridge while the analysis of our natural lead was made by the Lamont Geological Observatory from a piece of our specimen, *G*1. The average isotopic mass, M, of each specimen was computed from the relation

$$M=\sum M_i f_i, \tag{2}$$

where M_i is the mass of the ith isotopic species, and f_i is the fraction of lead atoms in the specimen which are of the ith species. With M defined as in (2), it can be shown that

$$\delta M=\sum \Delta M_i \delta f_i+\sum f_i \delta M_i, \tag{3}$$

where $\Delta M_i=M_i-M$, and the δ's signify the uncertainty to be expected in the various parameters. According to Stanford *et al.*,[11] the uncertainty, δM_i, in the masses of the pure isotopes is ±0.001 amu for all of the species present in these specimens. Thus $\sum f_i \delta M_i=\delta M_i \sum f_i$, and the total contribution to the uncertainty in M from the second term on the right of (3) becomes ±0.001 amu. A detailed calculation using the experimental δf_i's in Table I[12] yields the uncertainties in average mass listed in the table.

For the present experiment the most significant aspect of the error in average mass determinations is the magnitude of δM for each specimen in relation to the total available range in average mass number $(M_{\max}-M_{\min})$. The difference between the heaviest and lightest specimens in Table I gives $(M_{\max}-M_{\min})$ equal to 1.618 amu and the ratio, $\delta M/(M_{\max}-M_{\min})$, is listed in the last column. These values show a substantial variation from specimen to specimen which could undoubtedly be reduced if all the specimens could be analyzed at the same time and with the same instrument. Such a series of measurements is planned when all the low-temperature measurements on the specimens are completed. However, despite the variation in δM from the present data, the resolution within the available range of M is reasonably good for the present purposes.

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[11] Stanford, Duckworth, Hogg, and Geiger, Phys. Rev. **85**, 1039 (1952).

[12] In computing the δM the following expression was used to relate the δf_i to the atomic percentages, p_i, listed in the first four columns of Table I:

$$\delta f_i=[(\delta p_i^2)+(p_i^2\times 10^{-4})+(100-\Sigma\, p_i)^2]^{\frac{1}{2}}\times 10^{-2},$$

where δp_i is the uncertainty in p_i. The bias error from known sources of systematic error is estimated by Oak Ridge as less than 1% and is represented by the second term in the brackets. (No bias error was included in the analysis of 9*F* which was not an AEC specimen.) The third term was used to account for specimens where $\Sigma\, p_i\neq 100$ (e.g., specimen 138).

TABLE I. Purity and mass analysis of the specimens.

Specimen	Purity % Pb	Isotope 204	Isotope 206	Isotope 207	Isotope 208	$M \pm \delta M$	$\delta M/(M_{\max} - M_{\min})$
138	99.31	0.20 ±0.08	5.30±0.20	11.42±0.20	82.10±0.5	207.811±0.067	0.041
704	99.96	0.240±0.005	15.18±0.05	26.81±0.03	57.77±0.03	207.460±0.008	0.005
9F	99.998	1.347±0.004	25.21±0.03	21.18±0.04	52.26±0.08	207.271±0.002	0.001
702	99.84	5.30 ±0.04	36.46±0.05	21.54±0.08	36.71±0.03	206.884±0.011	0.007
258	99.48	0.5 ±0.2	71.3 ±1.0	5.1 ±0.5	23.1 ±1.0	206.543±0.030	0.019
581	99.88	25.70 ±0.08	33.77±0.04	14.30±0.03	26.23±0.08	206.193±0.013	0.008

b. Superconducting Transition Measurements

As described in the previous section, the total variation in M in the six specimens available to us is about 0.8% of the atomic weight of lead. If, for purposes of estimation, Eq. (1) is used with the value of $p = -0.5$, it is readily shown that the total variation to be expected in T_c is about 0.4%. For these lead specimens all the critical temperatures would be expected to lie within a temperature range of about 0.028K° located near 7.2°K. Since there are six specimens within this temperature range, the average temperature interval between individual specimens is of the order of 6×10^{-3} K°. In view of the well known difficulties associated with precision thermometry, especially in the range above the critical point of helium, the accurate measurement of such small temperature differences is a formidable experimental problem, and it was not attempted in this work.

The shift in critical temperature, ΔT_c, due to the isotopic mass implies a shift in critical field, ΔH_c, between two specimens when measured at the same temperature. The relation between ΔT_c and ΔH_c follows from the general relation

$$\frac{dT_c}{dM} = -\left(\frac{\partial H_c}{\partial M}\right)_{T=T_c(9F)} \Big/ \left(\frac{\partial H_c}{\partial T}\right)_{M=M(9F)}. \tag{4}$$

The slope of the critical field curve near T_c, $(\partial H_c/\partial T)_M$, was recently measured by Decker, Mapother, and Shaw and reported to be 240±2 gauss/°K.[13] From (4) it follows that $\Delta T_c = 0.028$°K corresponds to $\Delta H_c = 6.76$ gauss, or an average fieldwise separation between our specimens of the order of 1.35 gauss when measured at a constant temperature near T_c. Field increments of this magnitude can be resolved with fairly high precision. Magnetic measurements of the superconducting transition can be made with an absolute precision of the order of 0.02 gauss and so the crucial experimental consideration becomes that of maintaining the specimen temperature constant.

Fortunately it is possible to utilize the great temperature sensitivity of carbon resistance thermometers to achieve a temperature stability of the order of $\pm 10^{-4}$ K° for the periods of time necessary to make the comparison measurements between superconducting specimens. This short-time stability is, in our experience, at least an order of magnitude better than the precision with which absolute temperatures can be measured in this temperature range using carbon thermometers. The problem in making absolute temperature determinations arises from the necessity to extrapolate the thermometer calibration curve into a region where direct calibration is very difficult.

Pursuant to the general considerations outlined above, the measurements in this work consisted of a series of isothermal comparisons of H_c values between the specimens of different isotopic mass. The techniques used were practically the same as were employed in the recent pressure effect measurements on lead by Hake and Mapother,[14] to which the reader may refer for most of the experimental details.

The specimen holder used in these measurements is shown in Fig. 1. This holder was suspended inside a vacuum-tight container called the inner can in an atmosphere of helium gas to promote thermal equilibrium. The inner can, in turn, was suspended inside an outer can which was immersed in liquid helium. The pressure of helium gas in the space between the inner and outer cans was adjusted to provide the desired degree of thermal coupling with the liquid helium bath, and the temperature of the specimens was regulated by controlling the power to the heater on the specimen holder. The only important change in the present apparatus over that used in our previous work on the pressure effect was in the use of the massive copper yoke in the specimen holder shown in Fig. 1. This change increased the heat capacity, improved the thermal contact between specimens and thermometer, and provided a symmetrical location of the heating elements with respect to the thermometer, all of which factors contribute to easier temperature regulation and greater freedom from thermal gradients than was encountered in the earlier apparatus.

The applied magnetic field was aligned parallel with the long axes of the specimens and the transition from the superconducting to the normal state (always in this order to avoid difficulties with supercooling) was observed by using a sensitive ballistic induction method. The experimental quantity measured is the change in magnetic flux within the specimen for a known

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[13] Decker, Mapother, and Shaw, Proceedings of the Fifth International Conference on Low-Temperature Physics, Madison, Wisconsin, 1957. Edited by J. R. Dillinger (University of Wisconsin Press, Madison, 1958).

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

incremental change in the applied field. The observed galvanometer deflections, which are proportional to the flux changes, may be combined to give a parameter which we call the effective permeability, μ_e, of the specimen. The critical field of the specimen is obtained from a plot of μ_e *vs* applied field by extrapolating the μ_e curve to the value $\mu_e = 1$. A detailed discussion of this measuring method has been published.[15]

As many as five specimens could be placed in the apparatus at one time, the sixth search coil being used as a dummy in our method. However, at low temperatures where large critical fields are encountered, only three specimens were measured at one time since the distortion in field around a superconducting specimen results in an appreciable perturbing effect on the field at the adjacent position in the holder. There will be occasion to refer to this question in later discussion and for brevity we shall designate this phenomenon as the field interference effect (FIE). It is most easily avoided by leaving every other site in the holder vacant, since the magnitude of the FIE at next nearest neighbor sites is small enough to be disregarded at all values of H_c encountered in this work. At all temperatures the procedure was to make repeated measurements of H_c for each specimen in the holder while the whole assemblage was held at constant temperature.[14] Specimen $9F$ was measured as a comparison specimen on all of the experimental runs.

The measurements extended over a temperature range from about 7.2 to 1.3°K. The first measurements were made near 7°K since the nitrogen solenoid[15] then in service had an upper limiting field of about 100 gauss. Because of the large critical field of lead at low temperatures it was necessary to construct a new solenoid capable of producing fields up to the order of 1000 gauss. The new solenoid is based on the Garrett sixth-order system,[16] and, like the old solenoid which it supercedes, it operates immersed in liquid nitrogen and serves the same purpose in our measuring method. The new solenoid has a high-voltage winding, being designed for operation from a Varian *V*-2200*A* power supply which provides a highly stabilized current. It produces a field of about 1000 gauss with a terminal voltage of 708 volts and a power input of about 1 kw. The liquid nitrogen cooling has worked out very well.[17] The field distribution within the solenoid was measured with a pair of matched search coils and found to be homogeneous to better than 0.1% over the entire region occupied by the specimens. A nuclear resonance measurement also provided an accurate value of the gauss/ampere constant of the solenoid.

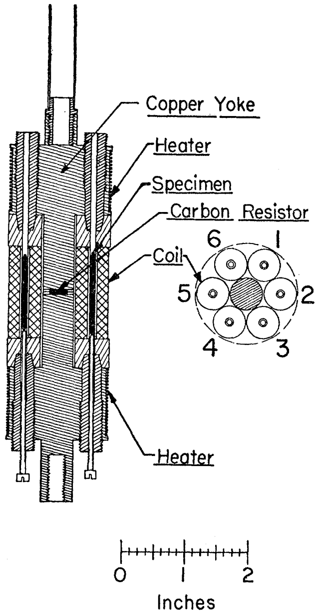

FIG. 1. Specimen holder assembly. This unit is suspended within the vessel called the "inner can" in the apparatus described in reference 14.

3. RESULTS

In presenting the results of these measurements we shall consider separately (a) the high-temperature data obtained at fields under 50 gauss near T_c, and (b) the lower-temperature data obtained after the strong solenoid was installed. This happens to be the order in which the data were actually measured, but it will also develop that an orderly discussion of the results favors this order of presentation.

a. Data at High Temperature

The first experimental run involved the comparison of the critical fields of specimens $9F$, $G1$, 704-1, 704-2, and 581. Specimens $9F$ and $G1$ were prepared from the natural lead sample, while specimens 704-1 and 704-2 were from AEC lot *FQ*-704(a). The inclusion of two pairs of specimens of the same mass was done to provide a direct check on the over-all consistency and resolution of the measuring method in determining the small critical field shifts which were to be expected. The results of these measurements are tabulated opposite I in Table II which contains the H_c value for the standard specimen ($9F$) and the differences in critical field ΔH_c between $9F$ and the other specimens. Since the significant datum of the comparison measurement is the difference in the critical fields, the symbol $\Delta H_c(X) = H_c(X) - H_c(9F)$ will be employed throughout the subsequent discussion to designate the difference in critical field between a specimen, X, and the standard specimen, $9F$, when both are measured at the same temperature. For brevity in the tabular values, H_c is

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

[16] M. W. Garrett, J. Appl. Phys. **22**, 1091 (1951).

[17] A minor problem worth mentioning is that the continual boiling of the liquid nitrogen tends to concentrate liquid oxygen in the bottom of the Dewar, since O_2 is the usual impurity in liquid N_2. In addition to exerting a very small effect on the resultant field of the solenoid (due to the paramagnetism of O_2), the presence of oxygen creates a combustion hazard at the solenoid. A special drain line is provided in our nitrogen Dewar to dump the contents periodically.

TABLE II. Result of measurements near T_c. The numbers in parentheses following each value of ΔH_c refer to the number of comparisons at each point. All these data were taken within 0.21°K of $T_c(9F)$.

Run	$H_c(9F)$ gauss	$\Delta H_c(581)$ gauss	$\Delta H_c(258)$ gauss	$\Delta H_c(702)$ gauss	$\Delta H_c(704\text{-}1)$ gauss	$\Delta H_c(138)$ gauss	$\Delta H_c(G1)$ gauss	$H_c(704\text{-}2)$ $-H_c(704\text{-}1)$ gauss
I	4.0 ± 0.1	$5.52\pm0.08(9)$			$-0.65\pm0.05(10)$		$0.05\pm0.04(4)$	$-0.03\pm0.04(1)$
I	18.2 ± 0.2	$5.42\pm0.17(8)$			$-0.64\pm0.04(9)$		$0.03\pm0.04(2)$	$-0.05\pm0.01(1)$
I	30.5 ± 0.1	$5.39\pm0.03(2)$			$-0.64\pm0.08(5)$		$0.00\pm0.06(1)$	$0.06\pm0.08(1)$
I	46.0 ± 0.1	$5.44\pm0.11(2)$			$-0.69\pm0.04(3)$		$-0.04\pm0.08(1)$	$0.05\pm0.05(1)$
II	3.0 ± 0.1	$5.52\pm0.02(8)$	$3.19\pm0.02(12)$	$1.66\pm0.03(15)$	$-0.61\pm0.03(7)$			
II	12.9 ± 0.1	$5.52\pm0.02(5)$	$3.11\pm0.01(5)$	$1.63\pm0.03(8)$	$-0.56\pm0.01(5)$			
II	21.3 ± 0.1	$5.59\pm0.08(6)$	$3.14\pm0.05(8)$	$1.65\pm0.06(6)$	$-0.59\pm0.05(8)$			
II	49.8 ± 0.2		$3.04\pm0.02(7)$	$1.54\pm0.05(6)$	$-0.57\pm0.03(5)$			
III	3.2 ± 0.1		$3.14\pm0.04(19)$					
III	10.1 ± 0.1		$3.15\pm0.02(9)$			$-2.05\pm0.05(12)$		
III	26.3 ± 0.1		$3.11\pm0.03(5)$			$-2.00\pm0.03(6)$		
Average ΔH_c at $H_c(9F)=0$		$5.55\pm0.10(40)$	$3.16\pm0.04(65)$	$1.65\pm0.05(35)$	$-0.63\pm0.06(52)$	$-2.06\pm0.05(18)$	$+0.01\pm0.06(8)$	$+0.01\pm0.06(4)$

given only for specimen $9F$. As was to be hoped, the specimens of the same M showed very small differences in H_c while significant differences in H_c were evident in the case of specimens of different M.

Runs II and III (also given in Table II) involved comparisons between $9F$ and other specimens of different M as noted. Run III was made after the installation of the strong solenoid and the agreement between the results of runs II and III provides an additional check on the consistency of the two solenoid calibrations.

To give an impression of the resolution achieved in the transition measurements, the experimental permeability curves at a particular temperature for all of the specimens have been shown in Fig. 2. As a consequence of the field homogeneity and temperature stability prevailing at the specimens, the transition breadth (with the exception of specimen 581) is in reasonable agreement with expectations based on the length to diameter ratio of the specimens. The accuracy of the determination of the slope of the μ_e cruves cannot be shown on the scale of Fig. 2, but it will be considered later in the discussion. The transition breadth in all cases is sufficiently narrow to permit a reasonably precise determination of ΔH_c.

Since specimen $9F$ was measured on all runs and all isotopes were compared against it, the measured values of ΔH_c for different specimens and different runs can be corrected to a single temperature as follows. A plot of ΔH_c *versus* $H_c(9F)$ was made and the best straight line (consistent with the similarity principle) drawn through the experimental points. The value of ΔH_c at the intercept of $H_c(9F)=0$ is then the value of ΔH_c for each isotope at the critical temperature of the $9F$ specimen. Figure 3 is such a plot and shows the linear dependence of ΔH_c upon $H_c(9F)$. The values of ΔH_c at $T_c(9F)$ are recorded in the last line of Table II and are plotted as ordinate against M as abscissa in Fig. 4. For each point the experimental uncertainty (mostly δM) is indicated by horizontal or vertical lines through the point. With the exception of the point for specimen 581 (which we shall ignore for the moment), the data fall along a straight line to within the accuracy of the measurements. From the slope of the line the value $(\partial H_c/\partial M)_T=-4.17\pm0.11$ gauss/amu is obtained.

Using Eqs. (1) and (4) it is readily shown that the exponent, p, may be expressed in terms of the measurable quantity

$$p=-\frac{M(\partial H_c/\partial M)_T}{T_c(\partial H_c/\partial T)_M}, \tag{5}$$

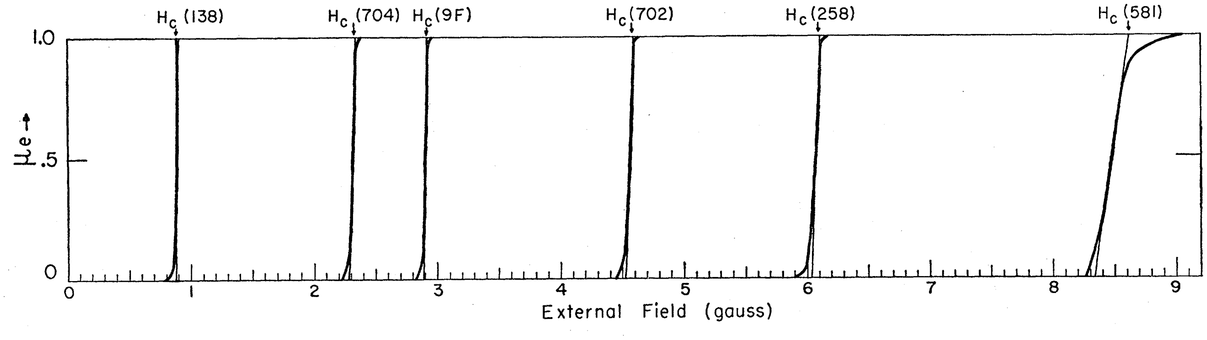

FIG. 2. Magnetic superconducting to normal transitions of the lead isotope specimens at a temperature 0.012K° below T_c for specimen $9F$. μ_e is the effective permeability of the specimen. Small arrows above each transition denote the H_c values determined for each specimen.

and substitution of

$$M=207.27 \text{ amu},$$
$$T_c=7.175\pm0.005\text{°K},^{18}$$
$$(\partial H_c/\partial T)_M=240\pm2 \text{ gauss},^{13}$$
$$(\partial H_c/\partial M)_T=-4.17\pm0.11 \text{ gauss/amu}$$

gives $p=-0.501\pm0.013$.

The foregoing calculation of the exponent, p, disregards the datum for specimen 581 on the grounds that its departure from the average behavior of the other five specimens is far outside the limits of the known experimental error. It will also be noted in Fig. 2 that specimen 581 has an anomalously broad superconducting transition. This circumstance and also the fact that all the specimens except specimen 581 supercool slightly were noted early in this work. On the supposition that the anomalies might be associated with some accident in the preparation of this particular specimen, it was run through the entire purification and recrystallization process a second time. Both the anomalies in ΔH_c and in transition breadth were observed with excellent reproducibility following the second processing, indicating that the magnetic measurements for this specimen are correct. The possibility of an error in the isotopic analysis was also considered and Dr. C. P. Keim of Oak Ridge kindly arranged for a new analysis of this specimen. The results essentially confirmed the original analysis. Thus from all the experimental evidence available to us at present, specimen 581, for obscure reasons, is clearly out of line with the other specimens, and we feel justified in leaving it out of consideration for the time being in interpreting these measurements.

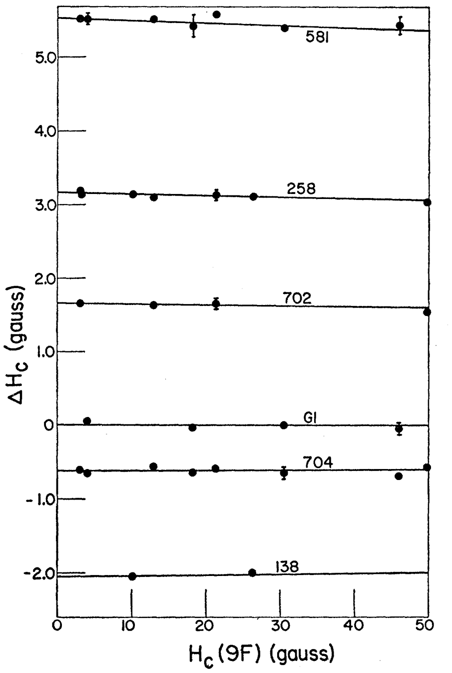

FIG. 3. Isotope shift near T_c. ΔH_c is the isothermal shift in critical field relative to specimen 9F. The lines shown represent the best fit to the experimental points consistent with the slope expected from the similarity principle. The intercept of each line at $H_c(9F)=0$ gives the isotope shift for that specimen at the temperature corresponding to T_c for specimen 9F.

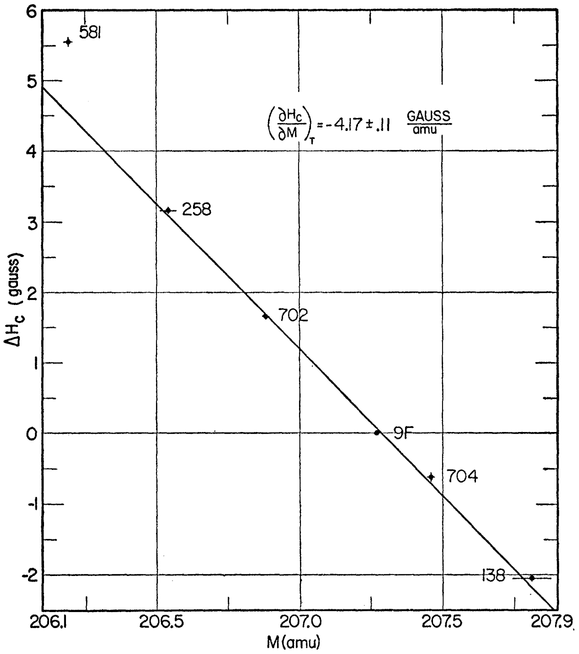

FIG. 4. Isotope shift, ΔH_c, *vs* average isotopic mass, M. ΔH_c is the isotopic shift relative to specimen 9F and evaluated for $T=T_c(9F)$. Probable error in the determination of ΔH_c and M for each specimen is indicated by the horizontal and vertical lines through each point. As explained in the text, the point for specimen 581 was disregarded in computing $(\partial H_c/\partial M)_T$.

b. Data at Low Temperature

The low-temperature measurements which have been made thus far consist primarily of comparisons between the three specimens 258, 9F, and 138. For the reasons mentioned in Sec. 2b it was decided to limit the number of specimens in the holder to three in order to avoid trouble from the field interference effect. Except for such complications as the FIE which are associated with the much larger values of H_c encountered at low temperatures, the low-temperature measurements are the same in principle as those described above, and they were made by the same method.

The results of these observations are listed in Table III. The data are remarkable in exhibiting a pronounced *increase* in ΔH_c with decreasing temperature, this being exactly opposite to the behavior to be expected on the basis of the similarity principle. In Fig. 5 the observed values of H_c for the three specimens are plotted against the square of the temperature as

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

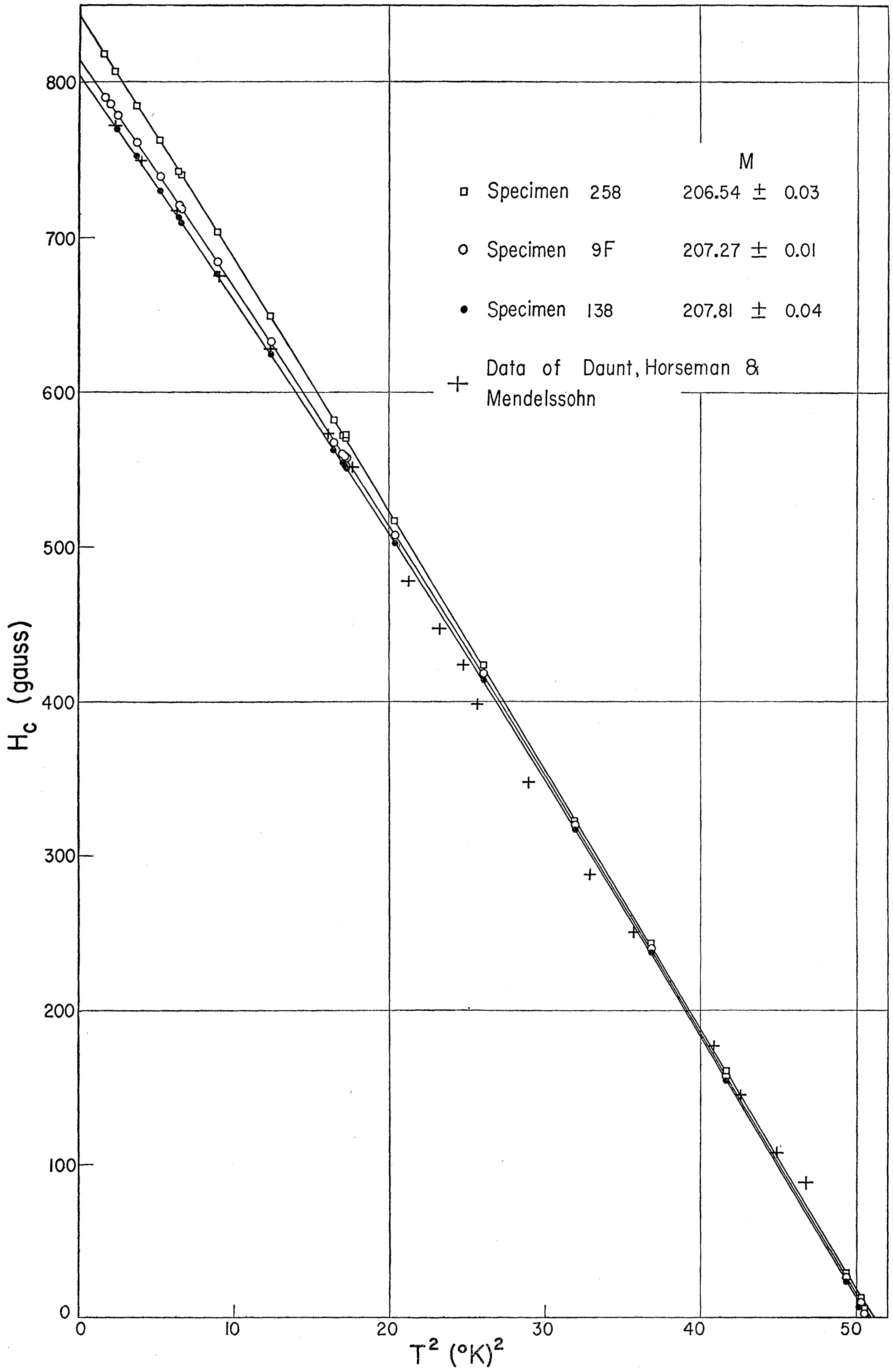

FIG. 5. Critical field, H_c, for three lead specimens of different average isotopic mass plotted against T^2.

TABLE III. Summary of results of low-temperature observations. Run IV differs from run III only in that the relative positions of the samples were altered.

$H_c(9F)$ gauss	$\Delta H_c(258)$ gauss	No. of obs.	$\Delta H_c(138)$ gauss	No. of obs.	T°K
			Run III		
158.0±0.1	2.74±0.03	5	−2.77±0.04	4	6.5 ±0.1
240.3±0.1	2.72±0.04	3	−2.33±0.04	3	6.1 ±0.1
320.4±0.2	2.53±0.14	5	−3.11±0.09	5	5.6 ±0.1
418.4±0.3	5.4 ±0.3	3	−3.8 ±0.1	5	5.1 ±0.1
508.0±0.2	9.2 ±0.1	3	−5.5 ±0.1	2	4.50±0.01
557.7±0.3	12.5 ±0.2	2	−5.9 ±0.1	1	4.14±0.01
558.4±0.4	12.8 ±0.3	1	−5.8 ±0.3	1	4.14±0.01
559.9±0.3	12.7 ±0.1	3	−5.9 ±0.3	3	4.12±0.01
567.5±0.5	14.1 ±0.4	4	−5.2 ±0.2	5	4.04±0.01
632.4±0.4	16.5 ±0.3	7	−8.1 ±0.5	5	3.51±0.01
684.4±0.4	19.3 ±0.3	7	−8.4 ±0.1	4	2.98±0.01
718.5±0.4	21.9 ±0.1	7	−8.9 ±0.1	5	2.56±0.01
720.5±0.4	22.1 ±0.1	1	−8.0 ±0.2	2	2.53±0.01
720.6±1.0	22.4 ±0.2	2	−8.6 ±0.2	1	2.53±0.01
739.2±0.3	23.2 ±0.2	1	−9.2 ±0.2	3	2.28±0.01
761.0±0.8	23.8 ±0.4	1	−8.7 ±0.2	3	1.92±0.01
778.5±0.4	28.3 ±0.2	3	−8.8 ±0.1	2	1.56±0.01
778.7±0.6	28.4 ±0.2	3	−9.9 ±0.3	5	1.33±0.01
790.2±0.6	28.0 ±1.5	3			1.29±0.01
			Run IV		
567.8±0.9	13.5 ±0.4	7	−5.6 ±0.1	5	4.04±0.02
662.2±0.4	19.7 ±0.4	3	−8.0 ±0.3	4	3.20±0.02
719.5±0.4	23.4 ±0.2	5	−8.9 ±0.1	5	2.54±0.02
778.4±0.5	29.4 ±0.6	6	−9.9 ±0.1	2	1.33±0.02

determined from the carbon thermometer on the specimen holder.[19] The increase in ΔH_c with decreasing T is clearly in evidence.

For comparison, the data of Daunt, Horseman, and Mendelssohn[20,21] on the superconducting transition in lead have been plotted with a suitable correction to allow for the temperature scale used in the earlier work.[22] As can be seen in Fig. 5, the agreement with the earlier data is good in the temperature range below the boiling point of helium, and less good at higher temperatures. Since both the Oxford measurements and our own were based on direct calibration against the vapor pressure of helium in the range below 4.2°K, the temperature determinations in the two experiments would be expected to show the greatest harmony in this region. Considering that M was unspecified in the Oxford measurements, the agreement in this temperature range between their data and the present work is considered quite satisfactory. The poorer agreement above 4.2°K is most probably associated with the determination of T in this experimentally difficult range. It is planned in future measurements to make a more serious effort to get better temperature determinations in this range.

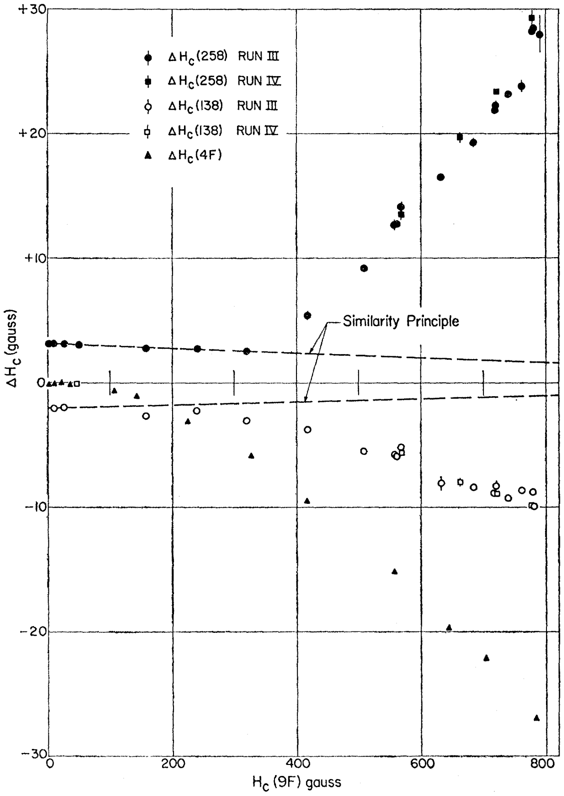

FIG. 6. Critical field shift, ΔH_c, *vs* H_c for the comparison specimen, $9F$. This abscissa is approximately equivalent to a T^2 scale but is independent of any inaccuracy in absolute temperature measurement. Dashed lines show the expected variation of the isotopic shift on the basis of the similarity principle. The large values of $\Delta H_c(4F)$ show that the low-temperature shifts are unrelated to the isotope effect since specimens $4F$ and $9F$ have the same isotopic mass.

The scale of Fig. 5 is too coarse to exhibit the detailed nature of the differences observed between the specimens. To show this difference with greater resolution, the experimental ΔH_c values are plotted against the critical field, $H_c(9F)$, as shown in Fig. 6. (This type of plot is independent of any error associated with our determination of the absolute temperature.) For comparison, the dotted curves give the expected ΔH_c assuming the validity of the similarity principle as explained in the caption of Fig. 6. The experimental results are in fair agreement with the similarity principle up to H_c values of about 350 gauss (about 5.5°K), but for greater H_c values (i.e., lower temperatures) the difference curves diverge rapidly down to the lowest temperatures of observation.

A number of the actual experimental transitions from

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[19] The present temperature determinations involved the calibration of the resistance of the carbon thermometer against the vapor pressure of liquid helium below 4.2°K, using the T_{55E} vapor pressure scale [Clement, Logan, and Gaffney, Phys. Rev. **100**, 743 (1955)]. The resistance-temperature relation was extrapolated to yield approximate temperatures above 4.2°K, since the initial purposes of this investigation did not require accurate knowledge of the absolute temperature.

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

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

[22] The data of Daunt *et al.*, as originally reported, were based on the 1932 vapor-pressure scale. So far as we are aware, these are the only measurements of sufficient completeness and accuracy available on lead to afford a significant comparison.

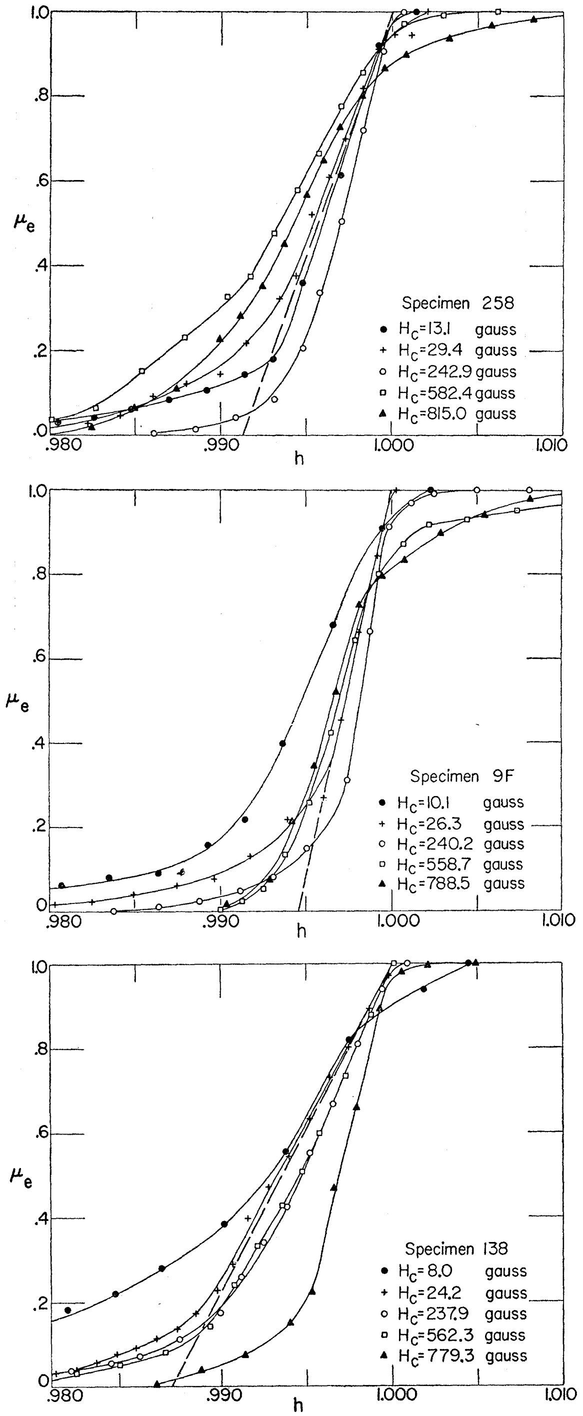

FIG. 7. Superconducting to normal transitions of three lead specimens at various temperatures plotted against reduced field, $h=H_e/H_c$. Note the expanded scale of h. Dashed lines indicate the transition shape for an ideal ellipsoid having the same length to diameter ratio as the actual specimen.

which the above critical-field shifts were obtained are shown in Fig. 7 where the effective permeability of the specimen, μ_e, has been plotted as a function of the reduced field, $h=H_e/H_c$. H_e is the applied external magnetic field and H_c is the critical field of the specimen determined by extrapolating the linear portion of the μ_e curve as discussed by Cochran, Mapother, and Mould.[15] For each specimen a representative sampling of transition curves at various values of H_c (i.e., various measuring temperatures) are shown. A noteworthy feature of the transitions when plotted against the reduced field is that they cluster about the slope to be expected on the basis of each specimen's demagnetizing factor. The inference from this observation is that over most of their volume the specimens are macroscopically homogeneous in their superconducting properties. (For example, gross inhomogeneities due to such causes as nonuniform strain would produce substantial broadening in the magnetic transition.)

The variation in relative transition width of specimen 258 appears to be without any recognizible pattern. However, both 9*F* and 138 show a small systematic trend with temperature. It will be noted that for both of these specimens the transition at the smallest H_c (nearest T_c) is the broadest, transitions at higher H_c values being generally sharper. More recent measurements on Pb (to be reported later) suggest that this is a characteristic feature of the magnetic transition, at least when measured by the present method. A similar but more exaggerated effect has been noted in measurements of Al.[15,23,24]

Another feature of the curves of Fig. 7 that deserves comment is the rounding tendency of the curves near $\mu_e=1$. The rounding appears to increase as H_c increases. From other experiments (to be reported later) it is suspected that this effect is correlated with the large anomalous shifts in ΔH_c and that the values of H_c for sample 138 are more characteristic of the intrinsic transition in Pb than the others in that the rounding is least pronounced for this sample. We think it probable that the large rounding of the transition curve of 581 (which, to date, has only been measured near T_c) is an accentuated case of the rounding in the transitions of 258 and 9*F* at low temperatures.

Superficially, the large deviations from the similarity principle shown in Fig. 6 look like an unusually large isotope effect in the sense that the large low-temperature ΔH_c shifts are in the same direction as the normal isotope shift observed near T_c. To check whether this behavior was due to the difference in isotopic mass, a control experiment was run at temperatures below 4.2°K with a different specimen, 4*F*, being compared with specimen 9*F*. Specimen 4*F* was prepared from the same lead sample as specimen 9*F* and had presumably the same *M*. To our surprise, the measurements below

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[23] J. F. Cochran and D. E. Mapother, Phys. Rev. **111**, 132 (1958).

[24] The transitions of Fig. 7 are plotted against a greatly expanded scale in order to show the observed shape in detail. It should be clear that these variations in transition breadth are so small that they have essentially no effect on the determination of H_c by the method used here.

4.2°K showed substantial differences in H_c between these specimens. The observed ΔH_c values for $4F$ are also shown in Fig. 6. It would seem from these observations that the departures from the similarity principle have nothing to do with the isotopic mass and that the correlation between ΔM and the anomalous ΔH_c values in the case of specimens 258 and 138 is fortuitous. It is interesting to note that the general character of the ΔH_c values observed for specimen $4F$ is the same as that shown by specimens 258 and 138.

Following the observations on specimen $4F$, this experiment was interrupted by a technical failure in part of the measuring apparatus. It is clear from these results that further study of the isotope effect at low temperatures must wait until further information can be obtained concerning the cause of the large shift in the critical field curves. A systematic investigation into the possible causes of this effect is in progress but has been delayed by the aforementioned technical difficulties. In view of this delay we have decided that it is appropriate to publish the results obtained thus far in this work.

c. Possibilities for Systematic Errors

One of the first thoughts suggested by these observations is that they represent some kind of systematic error in the measurements. It thus seems desirable at this point to record some of the possibilities of error which have been considered. Such results could arise due to uncertainty in the magnitude of the applied magnetic field at the position of the specimens due to any of the following three causes.

(*1*) *Incorrect current calibration of either solenoid.*—This seems unlikely in view of the fact that both of the solenoids were calibrated using the very accurate nuclear resonance technique. However, additional checks were made under the actual conditions of the measurements which verified the self-consistency of the current calibrations of the air and nitrogen solenoids.

(*2*) *Variation of the magnetic field at different positions of the specimen holder.*—This possibility was checked by repeating a set of observations with the solenoid rotated in several positions about its axis. In addition, a complete set of data at several temperatures below 4°K were taken after interchanging the positions of specimens 258 and 138.

(*3*) *The field interference effect.*—The FIE was scrutinized with particular care since it does produce an effect qualitatively similar to that actually observed. However, both calculations and direct measurements using the unoccupied search coils as field detectors showed the FIE to be negligibly small compared to the observed ΔH_c values at all values of H_c when alternate sites in the holder were left vacant.

None of these tests gave any indication of any trouble in the magnetic field determinations, and it is concluded that they are correct to the precision noted.

As mentioned in Sec. 2b, the precision of these observations depends on the maintenance of all the specimens at the same constant temperature during the interval required for the comparison measurements. Theoretically the anomalous shifts in H_c could be attributed to differences in temperature between the specimens. The improbability of the occurrence of temperature differences large enough to produce the observed ΔH_c values can be seen from the following argument. The anomalous ΔH_c values increase with decreasing T, and at the lowest temperatures of observation they are of the order of 20–30 gauss larger than they should be on the basis of the similarity principle. At these same temperatures $(\partial H_c/\partial T)$ is of the order of -40 gauss/K°. Thus temperature differences between the specimens of the order of $\frac{1}{2}$K° would be required to account for the observed anomalous shifts. We are unable to conceive of any mechanism capable of producing and maintaining such large temperature differences between the specimens under the experimental conditions. In addition to the design features of the specimen holder noted previously which tend to promote good thermal equilibrium between specimens, the measurements at the lowest temperatures were made with the specimens actually immersed in He II.

In the face of these considerations it is our present view that these measurements can only be interpreted as representing genuine differences in the superconducting properties of the measured specimens.

4. DISCUSSION

a. Results Near T_c

For five out of six specimens measured, the present observations on the isotope effect in lead are consistent with the relation, $T_c = \text{const} \times M^{-\frac{1}{2}}$, as predicted by the recent atomic theories of superconductivity. To this extent the present results may be said to be understood.

The sixth specimen, 581, is in definite disagreement with the theoretical expectation in showing a larger than average isotope shift. The nature of the deviation shown by our specimen, 581, is the same as that reported in the earlier results of Olsen[8] and could possibly have the same origin. An explanation of this anomaly has not been found as yet.

b. Results at Low Temperatures

Although the low-temperature measurements were intended to investigate the isotope effect and the validity of the similarity principle, it is our conclusion that the unusually large shifts in H_c described here are essentially unrelated to the isotopic masses of the specimens. The substantial ΔH_c values observed for specimens of the same isotopic mass ($4F$ and $9F$) are direct evidence that some parameter other than M is responsible. Several other instances of large ΔH_c values for specimens of the same isotopic composition have since been observed.[13] The fact that the H_c values for specimens 258 and 138 diverge from $H_c(9F)$ at low temperatures in the same direction as their isotopic shift near T_c must be regarded for the present as just a peculiar coincidence.

Some interesting (and puzzling) consequences would follow if the apparent deviations from similarity evident in Fig. 6 were in fact due solely to the difference in isotopic mass of the specimens. However, it seems clear that this is not the case. Since the isotopic mass is not the dominating factor in this effect, there is no basis for expecting the similarity principle to apply to these specimens at low temperatures.

Even though our observations rule out the isotopic mass as the causative factor, there seems little doubt that the large low-temperature shifts represent a genuine property of the specimens and are not the result of some error in the measuring method. In addition to the various checks described above we note that effects very similar to those observed in this work have been reported in previous measurements by Daunt[25] and more recently by MacDonald and Mendelssohn.[26] Both the magnitude of the shift and its dependence upon temperature agree very closely with the results described here. In both previous investigations the superconducting transitions were measured by techniques responsive to the electrical resistance of the specimen and the discrepancy between the resistive H_c values and those obtained in separate magnetic measurements[20] was discussed.

The complete similarity between our magnetic and the previous resistive observations strongly suggests that we are observing the same phenomenon and that it is a characteristic property of lead. We think it probable that the low-temperature shift in H_c is evidence that the superconducting properties of lead are unexpectedly sensitive at low temperatures to such secondary effects as strain and impurity. Measurements still in progress indicate that the anomalous ΔH_c values occur in transitions which despite their apparent sharpness are not thermodynamically reversible. There is also evidence that strain in the metallic lattice is one of the agencies responsible for the anomaly.[27]

In conclusion, we remark that the low-temperature data described here represent the results of the initial phase of a continuing investigation. Further reports on measurements currently in progress will appear later.

5. ACKNOWLEDGMENTS

We are greatly indebted to G. De Pasquali of this department for his essential contributions in reducing and purifying the enriched isotopic specimens used in this work. We wish to acknowledge the cooperation of Dr. C. P. Keim and his associates in the Stable Isotopes Division of the Oak Ridge National Laboratory in making the enriched isotopic specimens available to us and in cheerfully responding to our numerous inquiries regarding their analysis. Our thanks also go to Dr. L. C. Hebel and Professor C. P. Slichter for their equipment and assistance in the nuclear resonance calibration of the solenoids. The large solenoid required for this work was completed with the assistance of a grant from the Graduate College Research Board of the University of Illinois.

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[25] J. G. Daunt, Phil. Mag. **28**, 24 (1939).

[26] D. K. C. MacDonald and K. Mendelssohn, Proc. Roy. Soc. (London) **A200**, 66 (1949).

[27] Decker, Mapother, and Shaw, Bull. Am. Phys. Soc. Ser. II, **3**, 133 (1958).