

onances, we note that H_{eff} for the hcp phase is 5% higher than for the fcc phase. The various contributions to H_{eff} have been discussed,² and it is clear that small changes in the contributing terms could account for the magnitude of the difference observed. A proper calculation of this point seems lacking to date.

The origin of the smaller resonances at frequencies 3 and 4 has not yet been determined, but it is tentatively suggested that they are associated with stacking faults. Both growth and deformation faults are observed in hexagonal cobalt.⁶ Growth faults are sequences of three planes, and deformation faults are sequences of four

planes of cubic close packing within the hexagonal phase. If the identification of the smaller resonances with faulted material is correct, the resonance at frequency 3, nearer the fcc absorption, probably is associated with deformation faults; whereas, the resonance at frequency 4, nearer the hexagonal absorption line, is associated with growth faults. These possibilities are currently being investigated.

ACKNOWLEDGMENT

We are indebted to W. P. Wolf and M. B. Webb for helpful discussions.

PHYSICAL REVIEW

VOLUME 121, NUMBER 1

JANUARY 1, 1961

Isotope Effect in Superconducting Lead*

R. W. SHAW,[†] D. E. MAPOTHER,[‡] AND D. C. HOPKINS
Physics Department, University of Illinois, Urbana, Illinois

(Received July 18, 1960)

The present work is a continuation of earlier measurements of the difference in critical fields of superconducting Pb specimens with various isotopic masses. The isotope samples have been repurified and the low-temperature behavior is now more fully understood. The results near T_c are consistent with the relation $T_c = \text{const} \times M^p$, where M is the average isotopic mass, and yield a value $p = -0.478 \pm 0.014$. The measurements at lower temperatures confirm the similarity principle to within approximately 0.1% and indicate that γ , the coefficient in the normal electronic specific heat, is independent of isotopic mass to a similar accuracy.

INTRODUCTION

THE isotope effect for a superconductor is usually discussed in terms of the shift in critical temperature T_c , resulting from variation in the average isotopic mass, M . Both theory¹ and experiment² agree in the result that $T_c = \text{const} \times M^p$ which is valid for isotopic mixtures of a given superconducting element. A value of p close to -0.5 is well confirmed for all elements for which measurements have been made.^{2,3}

Study of the isotopic shift in the critical field H_c , at temperatures below T_c presents special problems in the case of lead. As shown recently,^{4,5} this element is particularly susceptible to a type of hysteresis in the magnetic transition which obscures the determination

of H_c and complicates the measurement of the rather small isotopic shift.³

The results described here were obtained after repurification of the same isotopically enriched Pb specimens whose properties have been described in earlier reports,^{3,4} together with one new sample. Some of the ambiguities of the earlier data have now been removed.

EXPERIMENTAL

The apparatus and techniques were largely those of the earlier papers to which the reader is referred for details.^{3,4} Ballistic induction measurements were made over the range from T_c (7.175°K) to 1.2°K. Because as many as five specimens were in the cryostat simultaneously, correction was made for the field interference effect (i.e., the distortion of the applied field at one specimen caused by the presence of other superconducting specimens in the vicinity).³ This could be done exactly if the magnetic state of the other specimens was well known. However, there was some indication of flux trapping by two of the specimens which could not be precisely determined by the present method and so led to an uncertainty in this correction.⁶ The best available estimate of the extent of flux trapping came from a com-

* This work has received partial support from the Office of Ordnance Research, U. S. Army.

[†] Present address: Physics Department, Rensselaer Polytechnic Institute, Troy, New York.

[‡] Alfred P. Sloan Fellow.

¹ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **112**, 1175 (1957); hereafter referred to as BCS.

² B. Serin, *Progress in Low-Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1955), Vol. I, p. 142.

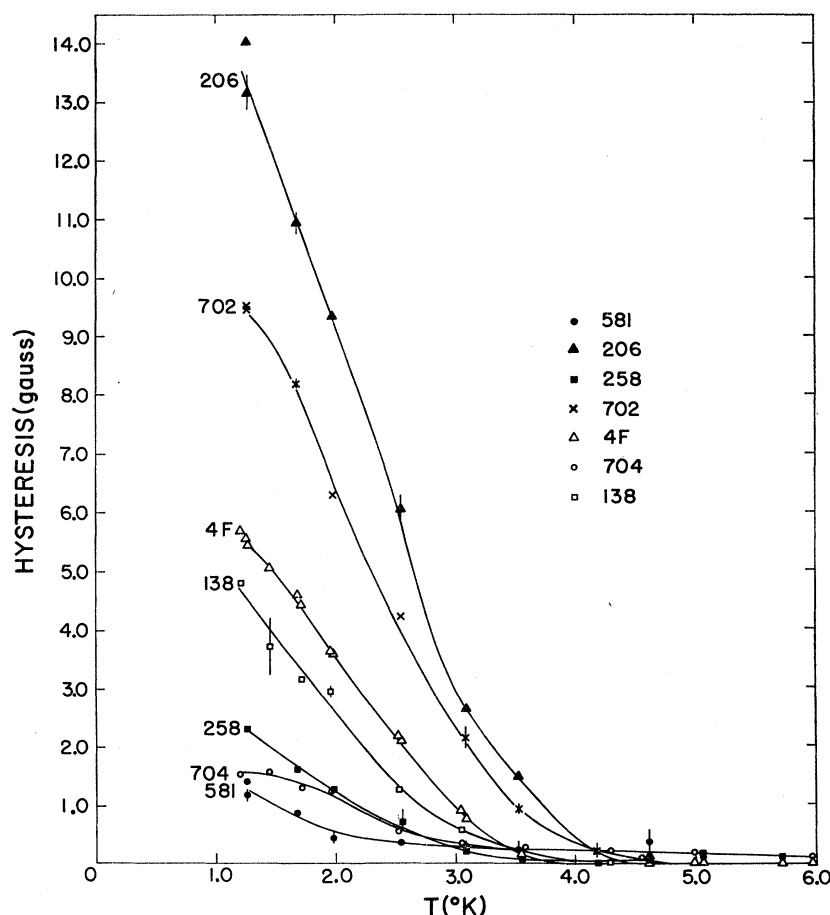
³ R. R. Hake, D. E. Mapother, and D. L. Decker, *Phys. Rev.* **112**, 1522 (1958).

⁴ D. L. Decker, D. E. Mapother, and R. W. Shaw, *Phys. Rev.* **112**, 1888 (1958).

⁵ R. W. Shaw and D. E. Mapother, *Phys. Rev.* **118**, 1474 (1960).

⁶ Flux trapping here refers to that flux remaining in the sample when the applied field is lowered to roughly $0.8H_c$, the lowest field normally reached between transitions in these measurements.

FIG. 1. Total hysteresis widths observed in the ballistic transitions of the isotope specimens.



parison of the demagnetizing factors calculated from the specimen geometry and from observed transition widths. This estimate, which indicated 50% flux trapped for specimen 702, 60% for 206, and approximately zero for the others, was used in making the correction and resulted in an uncertainty in the critical field differences of perhaps $0.0002H_c$.

Another uncertainty of this order was introduced by the correction for inhomogeneity in the solenoid field, approximately $4(\pm 1) \times 10^{-4}H_c$. By far the largest corrections to the results arose from the hysteresis which occurs in the superconducting transition of lead at $T/T_c < 0.5$. This phenomenon will be discussed below.

The isotope specimens of the earlier papers^{3,4} were repurified and analyzed by the Isotopes Division of the Oak Ridge National Laboratory. Their spectrographic analysis now places an upper limit on the metallic impurity in four of the specimens (258, 704, 702, 138) of approximately 0.05%. Although an analysis of the specimen labeled 581 was not carried out, it was purified in the same manner as the other four, and can reasonably be expected to have a similar impurity content.

One new specimen (identified hereafter as 206) has been added to those already measured. This is a radioactive specimen consisting of 88.3% Pb^{206} , 8.64% Pb^{207} ,

3.04% Pb^{208} , <0.1% Pb^{204} , and metallic impurity of less than 0.1%. This sample was interesting because its average isotopic mass is very close to that of sample 581, although it has a much different mass spectrum.

Following repurification and analysis, all of the isotope specimens were cast and grown as nearly single crystals. This was done in pure graphite crucibles which were carefully cleaned and outgassed prior to use. The entire high-temperature process was carried out in a vacuum of 10^{-5} mm Hg or better. The crucibles were then broken away from the samples and the samples annealed prior to measurement.

The natural lead specimen (4F) is the same one used by Decker *et al.*⁴ in the accurate determination of the critical field curve for lead. Spectrographic analysis of a section taken from this specimen showed less than 0.002% metallic impurity. Specimen 4F was used as a standard to which all other samples were compared.

Hysteresis is always present in the superconducting transition of lead well below T_c . However, recent investigations have shown that the reversible transition lies midway between the S-N and N-S transitions of a hysteretic specimen and have thereby provided a means of correcting for this behavior.^{4,5} All of the specimens

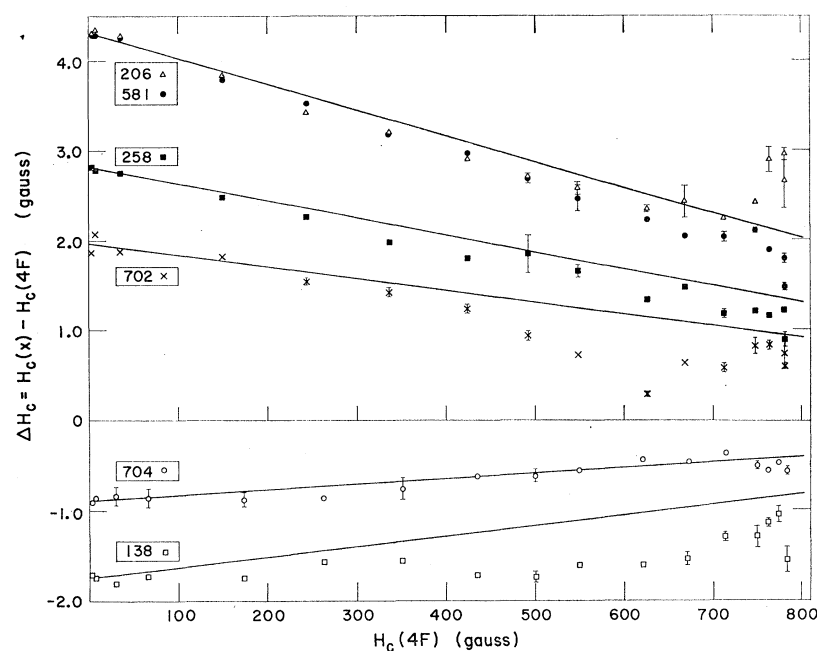


FIG. 2. Critical field differences between the isotope specimens and the $4F$ natural Pb sample vs the critical field of $4F$. The lines represent the similarity principle (see text).

were annealed prior to measurement to reduce the hysteresis to a minimum. The resulting hysteresis width is plotted vs temperature in Fig. 1. At the lowest temperature the hysteresis correction ($\frac{1}{2}$ of the transition width) varies from almost 7 gauss for 206 to less than 1 gauss for 581 and 704. The accuracy of the thermodynamic transition determined according to our method of hysteresis correction cannot be checked to better than about 5% of the hysteresis width. However, this correction is not serious above about 3°K ($H_c=670$ gauss) so that only conclusions which depend on the low-temperature results (such as determinations of shifts in γ and H_0) are affected.

Although it is now known that the hysteresis can be caused either by certain impurities or by mechanical strain, no treatment is yet known which will eliminate it reliably in a group of several specimens. The wide range of hysteresis shown in Fig. 1 for seven specimens (six of which had essentially the same chemical and metallurgical history) shows the problem very clearly. In view of the small amounts and precious nature of the isotopically enriched specimens, it is questionable whether the results of further improvement in the specimens would justify the additional effort entailed.

RESULTS

The results, after application of all known corrections, are shown in Fig. 2. As mentioned earlier, the critical fields of the isotopes are compared to that of the standard $4F$ sample at the same temperature. The data are then best represented as critical field differences plotted as a function of the standard specimen critical field as is done in Fig. 2. The lines drawn on the plot repre-

sent the so-called "similarity principle"⁷ which will be more fully discussed below.

In the region near T_c all corrections become small relative to the experimental scatter. (Where this is larger than the point size, it is indicated by a vertical line.) Thus, the points near $H_c(4F)=0$ are the most certain ones on the figure. They are, however, significantly shifted from those reported in reference 3 in almost all cases.

From the measured field shifts at the critical temperature of specimen $4F$, the shifts in T_c of the various specimens may be computed with the following results: 581(-5); 258(-2); 702(+1); 704(-1); and 138(+2). The number in parentheses following the specimen number give the shift in T_c from the values of reference 3. The shift is expressed in millidegrees and rounded off to the nearest integer because of the limitations on the accuracy of this comparison. It is noteworthy that shifts of both sign occur, with only specimens 702 and 138 showing an increase in T_c . (Additional effects to be described below give further evidence that specimens 702 and 138 differ slightly from the others.)

Presumably the main difference between the results in the present measurements from those of reference 3 is the chemical purification to which the specimens were subjected. Serin and co-workers have shown that shifts in T_c of the order of 10 millidegrees can occur in tin,⁸ indium, and aluminum⁹ at impurity concentrations of 0.1% or less. While there are at present no systematic

⁷ J. M. Lock, A. B. Pippard, and D. Shoenberg, Proc. Cambridge Phil. Soc. **47**, 811 (1951).

⁸ E. A. Lynton, B. Serin, and M. Zucker, J. Phys. Chem. Solids **3**, 165 (1957).

⁹ G. Chanin, E. A. Lynton, and B. Serin, Phys. Rev. **114**, 719 (1959).

data on this effect in lead, the large impurity limits on the specimens in the earlier work (up to 0.7%) could result in shifts in T_c of the size observed here if a corresponding effect is, in fact, characteristic of lead. But while the order of magnitude of the shift is compatible with the results of Serin *et al.*, the variation in direction of the shift between specimens is not. In all cases the dilute impurity studies have shown an initial reduction of T_c with increasing impurity addition. From this result a uniform increase in T_c for all the purified lead specimens would be expected in the present measurements, a condition which is evidently not fulfilled.

While there is no question of the competence of the present measurements to resolve H_c shifts of the size reported here, it should be emphasized that (a) the implied critical temperature shifts are really quite small, and (b) the extent of present knowledge on the impurity situation does not warrant an unequivocal assignment of the observed results to an impurity effect, even though it seems most plausible. The one point which can be made without qualification is that accurate determination of the exponent in the isotope effect requires very high specimen purity when so little variation in M is possible.

The intercepts at $H_c(4F)=0$ (Fig. 2) have been plotted vs the average isotopic mass of each sample in Fig. 3. The slope of this line yields

$$(\partial H_c / \partial M)_{T=T_c(4F)} = -3.80 \pm 0.15 \text{ gauss/amu.}$$

This value can be used to calculate the exponent, p , of the isotope effect by means of the equation³

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

where the partial derivatives are evaluated at T_c . The most recent values for the other constants of lead in this equation are

$$M = 207.27 \text{ amu,}$$

$$T_c = 7.175 \pm 0.005^\circ \text{K},^{10}$$

$$(\partial H_c / \partial T)_M = -238.4 \pm 1.2 \text{ gauss/}^\circ \text{K}.^4$$

Using these values yields $p = -0.461 \pm 0.025$. This value differs from that found in reference 3 ($p = -0.501 \pm 0.013$) almost entirely because of the new value for $(\partial H_c / \partial M)_T$. The best fit to the data of the earlier experiment (206 and 581 were not considered) is shown as a dashed line in Fig. 3, and it is apparent that the observed changes have not been large.

Note that the points for samples 702 and 138 in Fig. 3 lie conspicuously above a line which passes through the other points. If these two specimens are considered separately from the others, values of p can be calculated for each group:

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

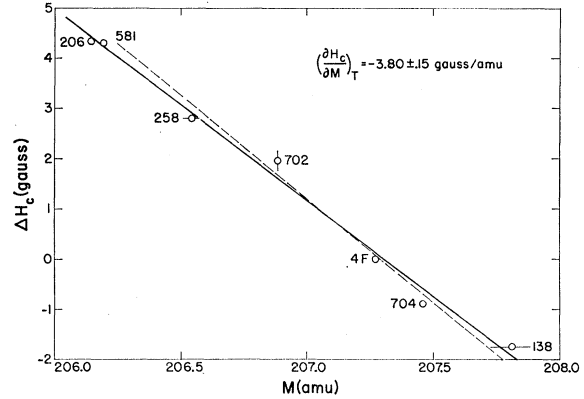


FIG. 3. Critical field differences of Fig. 2 extrapolated to $H_c(4F)=0$ vs average isotopic mass. The dashed line represents the best fit to the data of reference 3.

$$p = -0.478 \pm 0.014 \text{ (specimens 206, 581, 258, 4F, and 704),}$$

$$p = -0.480 \pm 0.30 \text{ (specimens 702 and 138).}$$

Such a division is entirely empirical, but it will be shown below that the low-temperature behavior of specimens 702 and 138 is also somewhat anomalous. Thermal conductivity measurements now in progress should show whether a separation based on differences in impurity content is justified.

DISCUSSION

The BCS theory of superconductivity predicts a value of $p = -0.500$ for all superconductors.¹ Recently Swihart has raised the possibility that the Coulomb interaction cutoff may not be exactly that used in the BCS theory.¹¹ His calculations lead to a value of the exponent somewhat smaller in magnitude than the BCS value and different for different superconductors. While this theoretical point appears to be somewhat conjectural at the moment, the present results agree more closely with the Swihart prediction for lead (-0.475) than with the BCS value.

The results at temperatures below T_c can be discussed in terms of the "similarity principle." As put forward by Lock, Pippard, and Shoenberg,⁷ this "principle" is essentially a statement of two conditions:

- (i) $H_0(M)/T_c(M) = \alpha$, a constant;
- (ii) $H_c(M) = H_0(M)f(t)$,

where $t = T/T_c$ and M = average isotopic mass. If α in (i) and $f(t)$ in (ii) are the same for two isotopically different specimens of the same superconducting element, these specimens exhibit the property of similarity (i.e., a geometrical similarity of critical field curves). On thermodynamic grounds it may be shown that the property of similarity implies invariance of γ with changes of M , where γ is the temperature coefficient

¹¹ J. C. Swihart, Phys. Rev. **116**, 45 (1959).

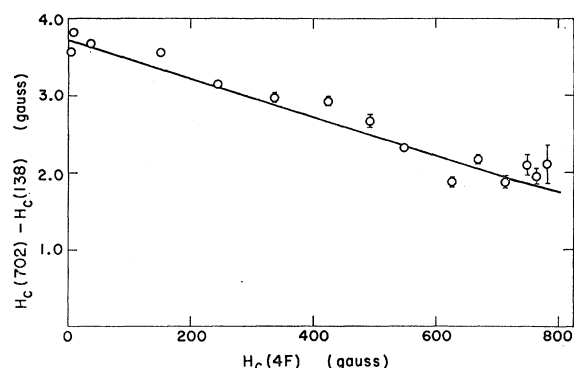


FIG. 4. Critical field differences between specimens 702 and 138 vs $H_c(4F)$. The line represents the locus of points expected on the basis of the similarity principle.

of the normal electronic specific heat.⁷ Insensitivity of γ to variation of M is also to be expected on physical grounds.

In Fig. 2 lines based upon the similarity principle have been drawn using the intercepts at $H_c(4F)=0$ and the critical field curve of the $4F$ specimen as reported in reference 4. These lines are the loci of ΔH_c values to be expected if the similarity principle were rigorously obeyed. However, the present data show that only specimen 704 does not deviate from this behavior in a systematic way. For fields below $H_c(4F)=670$ gauss (where the hysteresis is not important) specimens 581, 206, and 258 show small but systematic deviations from the expected behavior. The deviations are very much alike for all three specimens and, in fact, within the experimental scatter they are reasonably similar throughout this range.

This leaves only 702 and 138 as samples which deviate considerably from similarity with $4F$ and for these two specimens the deviations are also much alike. These specimens were measured on different runs and therefore at somewhat different temperatures. Thus, comparison between them must be made by reference to the standard specimen, $4F$. Figure 4 has been constructed to permit their direct comparison. It is apparent that similarity is reasonably well obeyed between these two specimens. This "mutual similarity" (together with the small deviations for 702 and 138 shown in Fig. 3) provides an empirical basis for considering them separately from the remaining specimens.

The deviations from similarity do not appear to be systematically dependent upon isotopic mass. (The deviations in Fig. 2 at fields above 670 gauss must be attributed to uncertainty in the hysteresis correction until it can be more accurately verified.) However, assuming that such deviations are real properties of the

specimens independent of hysteresis, it is possible to put upper limits on $(1/\alpha)(d\alpha/dM)$ and $[1/f(0)][df(t)/dM]$ of approximately 0.0005 per amu.

It is well known that γ is given by the expression¹²

$$\gamma = -\frac{V}{4\pi} \lim_{T \rightarrow 0} \left[\frac{H_c}{T} \left(\frac{dH_c}{dT} \right) \right],$$

and thus is sensitive to the detailed shape of the critical field curve at low temperatures. However, assuming that the low-temperature behavior in Fig. 2 is real, one finds $(1/\gamma)(d\gamma/dM) = -0.003 \pm 0.007$ per amu. If, on the other hand, points for which the hysteresis is greater than 2 gauss are completely ignored and a linear extrapolation is made on Fig. 2, a value of $(1/\gamma)(d\gamma/dM) = +0.00015 \pm 0.0008$ per amu is found. The quoted uncertainties are one standard deviation and do not reflect any estimate of the maximum uncertainty. It seems clear that, within the accuracy of the experiment, we have found no dependence of γ upon M .

The possibility that the isotope effect in lead might be sensitive to the detailed character of the mass spectra of individual specimens was suggested by the anomalous behavior of 581 in the earlier measurements.³ This conjecture was based on the fact that the mass analysis of 581 (25.8% Pb^{204} ; 33.9% Pb^{206} ; 14.2% Pb^{207} ; and 26.1% Pb^{208}) was conspicuously broader than any of the other specimens. The analysis of 206 (see the Experimental section) shows the most sharply peaked mass distribution of all the specimens measured.³

The intervening treatment of 581 (presumably the chemical refinement) converted it into one of the best behaved specimens of this series, particularly with respect to hysteresis (see Fig. 1). The divergence in Fig. 2 between 581 and 206 at the lowest temperatures is almost certainly related to the large hysteresis correction required by 206. Over most of the temperature range agreement between these specimens is very good. This result seems to dispose of the possibility that the isotope effect in lead has any appreciable sensitivity to details of the isotopic mass distribution. Because of the wider range of M available, more conclusive results on this point could be obtained with tin if it were deemed of interest.

ACKNOWLEDGMENTS

Our thanks go to D. K. Finnemore for his assistance in the laboratory and to Dr. M. Garfinkel for many illuminating discussions.

¹² J. G. Daunt and K. Mendelssohn, Proc. Roy. Soc. (London) **A160**, 127 (1937); also, J. G. Daunt, A. Horseman, and K. Mendelssohn, Phil. Mag. **27**, 754 (1939).