The Isotope Effect in Superconductivity. I. Mercury*

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The critical magnetic fields of various isotopic mixtures of mercury have been measured as a function of temperature. The critical magnetic field at any temperature is found to decrease with increasing average mass, and the critical temperature also decreases with increasing mass. The relationship $M^{\frac{1}{2}}T_c=$const, connecting the critical temperature T_c and the average mass number M, is established. Conclusions are drawn concerning the specific heats of the normal and superconducting states of the isotopes.

1. INTRODUCTION

THE observation that the critical temperature of superconductors varies with isotopic mass, was made originally by workers in this laboratory[1] and by Maxwell.[2] This result has been confirmed[3–5] despite the negative results reported by earlier workers.[6,7] The experimental evidence indicates that the critical temperature, T_c, and the average isotopic mass number, M, are connected by the relation $M^{\frac{1}{2}}T_c=$const. This relation lends support to theories developed by Frohlich[8] and Bardeen[9] which take the view that superconductivity is caused fundamentally by an interaction between the electrons in a metal and the vibrations of the crystal lattice.

Because of the interest in this discovery, we have published most of our results in abbreviated form;[10–12] and it is the purpose of this paper to present the details of our experimental techniques and a compilation of the data.

2. EXPERIMENTAL APPARATUS AND METHOD

(a) Samples

The samples of mercury used in these experiments, which had isotope distributions differing from the distribution occurring in nature, were obtained from the AEC.[13] The metal had been enriched in isotopes by electromagnetic separation and was purified by triple distillation. The natural metal was purified by us by double distillation. The average mass numbers of the various samples used in the experiments are listed in Table I in Sec. III.

The samples were prepared by sealing the mercury under helium gas in thin-walled glass capillary tubes. Samples 1, 2, 3, and 4 had a diameter of about 0.5 mm and were about 3 cm long; and samples 5, 6, and 7 had the same length, but were about 0.8 mm in diameter. The wall thickness of the capillary tubing was about 0.2 mm.

(b) Apparatus

The general arrangement of the samples, the helium flask and other relevant equipment is shown in Fig. 1.

Each sample was placed in a plastic coil form 2.5 cm long and 2.5 mm in diameter. Four thousand turns of Formex coated B & S gauge No. 44 copper wire were wound on each form. Five coils, C, standing vertically,

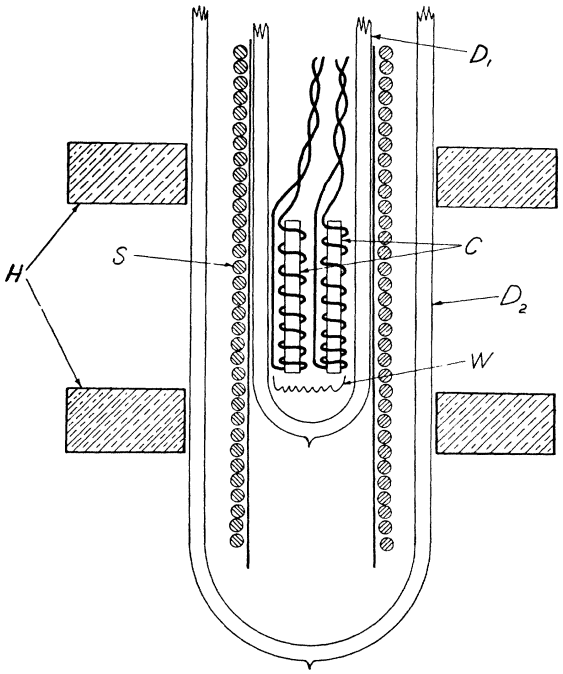

FIG. 1. The general arrangement of the apparatus. D_1 the liquid helium flask, D_2 the liquid nitrogen flask, C the sample coils, W the heater, S the solenoid, and H the Helmholtz coil.

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[13] The isotopes were produced by Carbide and Carbon Chemical Division, Oak Ridge National Laboratory, Y-12 Area, Oak Ridge, Tennessee; and were obtained on allocation.

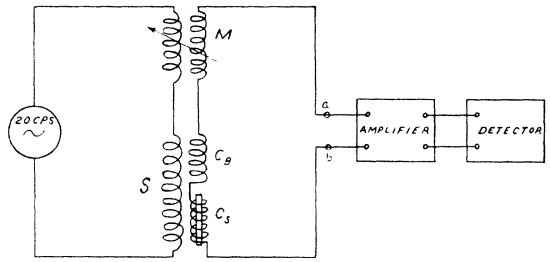

FIG. 2. Circuit for susceptibility measurement.

were arranged in a compact circle centered in the liquid helium Dewar flask, D_1. One coil was left empty. A non-inductivity wound heater coil, W, was placed below the sample coils. A solenoid, S, surrounded the helium flask, and both the flask and solenoid were centered in a second Dewar flask, D_2, which contained liquid nitrogen. The outer flask in turn was centered in a large Helmholtz coil, H.

The Helmholtz coil produced a magnetic field that was uniform to 0.1 percent over the volume occupied by the samples. A standard resistance was connected in series with the coil, so that the current flowing through the coil could be determined with an accuracy of 0.1 percent by measuring the potential drop across the resistance with a potentiometer. The flasks, solenoid and Helmholtz coil were mounted so that their common long-axis was along the direction of the earth's magnetic field. The orientation of the apparatus could be adjusted so that with the proper current flowing in the Helmholtz coil, the earth's magnetic could be canceled to give a net magnetic field over the samples of less than 0.01 oersted. The runs were made with the apparatus in this orientation, and the current value for canceling the earth's field, was then subtracted from all readings of the current in the Helmholtz coil, when the magnetic field at the samples was calculated. The Helmholtz coil could produce a maximum field of 150 oersted.

The solenoid, S, was 2.5 inches in diameter and 20.6 inches long, and had two separate windings. The samples were located at the geometric center of the coil. The outer winding consisted of fine wire and carried a small ac to provide an alternating magnetic field at the samples. The inner coil had heavy windings; it carried dc and was used when fields greater than 150 oersteds were required. The dc through the solenoid was then usually fixed at some value; and the field could be varied in a given range by changing the current in the Helmholtz coil. The current flowing in the solenoid was also determined by measuring the potential drop across a standard resistance connected in series with the coil. With this arrangement magnetic fields up to 300 oersteds were easily obtained.

(c) Critical Field Determination

The critical magnetic fields were determined by measuring the magnetic susceptibility of the samples as a function of the field. The method that we used to measure susceptibility has been carefully investigated by Shoenberg[14] and the arrangement of the components of our particular circuit is shown in Fig. 2.

The leads from each of the five coils in the helium Dewar flask were brought out of the flask through a standard multiple-connector. This arrangement permitted each sample coil C_S, in turn to be connected in series opposition to the empty coil C_B. The two coils formed the secondary of a mutual inductance, the outer winding of solenoid, S, constituting the primary. The solenoid was fed by a 20 cps alternating current signal generator; the current was adjusted to produce a magnetic field of 0.8 oersted amplitude at the samples. M is a small variable mutual inductance.

The voltage appearing across $a-b$ was amplified by a Ballantine decade amplifier and detected by a General Radio wave analyzer. The latter instrument was tuned to 20 cps and had a band width of 4 cps, thereby eliminating most noise and the extraneous 60 cps signal picked up from the power lines.

The measurements were made in the following manner. With no magnetic field in the Helmholtz coil, and the sample in the superconducting state, the mutual inductance, M, was adjusted to give a minimum signal in the detector. The magnetic field was then increased. When the field approached the critical value, the detected signal began to increase; and with a further increase in field, the signal passed through a maximum

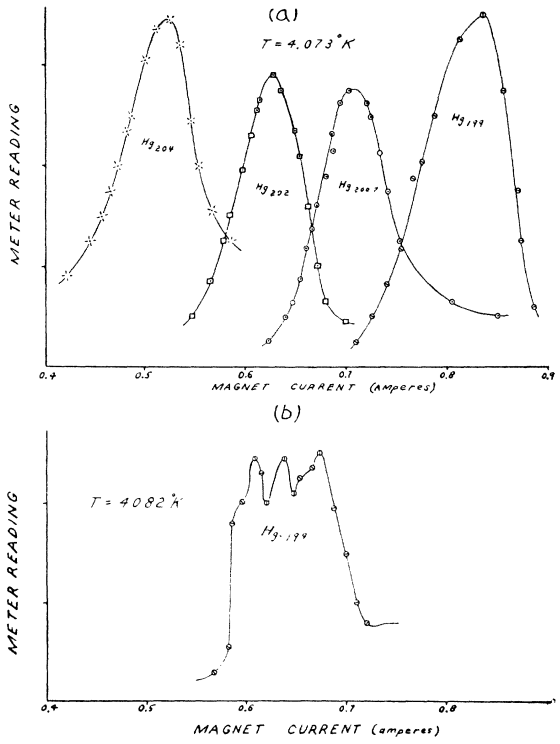

FIG. 3. Curves of detected signal *vs* current in the Helmholtz coil.

[14] D. Shoenberg, Proc. Cambridge Phil. Soc. **33**, 559 (1937).

value and finally reached a small steady value. The magnetic field value corresponding to the maximum was taken to be the critical field at a given temperature

The change in detected signal with magnetic field is the result of the transition of the sample from the superconducting state to the normal state. In the former state no magnetic field penetrates into the volume of the sample, whereas in the normal state the magnetic field passes through the whole volume. The peak signal corresponds to the magnetic field at which there is the greatest rate of change of susceptibility with field.

At 20 cps the ratio of sample radius to ac skin depth in the normal metal is less than 0.3. Thus, in these experiments there was negligible signal from the imaginary part of the susceptibility. The calculated power dissipated in the samples is also negligible.

In all the runs, we had three samples of isotopes and one sample of natural metal in the Dewar flask. At any given temperature, the critical magnetic fields of all four samples were determined as rapidly as possible. After a preliminary check that the shape of the curves of signal *versus* magnetic field were reasonably narrow and smooth, the values of the Helmholtz coil current corresponding only to the peak signal for the different samples were measured. The curve shapes were checked again in detail at three or four different temperatures.

The temperature was varied by pumping on the liquid helium bath and was kept constant by controlling the pumping speed with a Wallace and Tiernan manostat. The vapor pressure of the helium bath was measured with a mercury manometer. When the pressure was fixed, the variations were checked with a differential oil manometer. The manostat required very little manual adjustment to hold the vapor pressure constant to 1 mm of oil or about 0.1 mm of mercury. At all temperatures above 2.2°K, about 10 mw were dissipated in the heater coil to keep the liquid helium in temperature equilibrium. The vapor pressure-temperature scale used in this paper is the Mond Laboratory Scale of 1949.

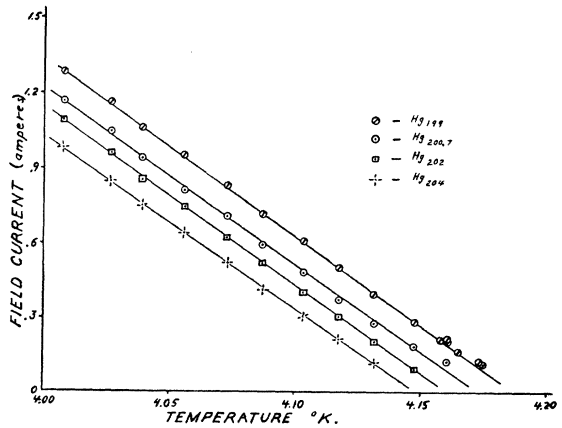

FIG. 4. Critical magnetic field *vs* absolute temperature of different isotopes.

TABLE I. The critical temperatures, T_c, as a function of average mass numbers M. Mass number 200.7 is natural mercury.

Sample No.	M	T_c °K
1	199.5	4.185
2	199.7	4.184
3	200.7	4.173
4	202.0	4.159
5	202.0	4.160
6	203.2	4.146
7	203.4	4.146

3. EXPERIMENTAL RESULTS

A typical set of curves of detected signal as a function of Helmholtz coil current are shown in Fig. 3(a). The width of the curves is about 3 oersteds, which is about twice as great as the theoretical width indicating that the width of the magnetic field transition was one or two oersteds. However, the change in critical magnetic field with average isotopic mass is clearly resolvable. There is a systematic increase in critical field with decreasing mass. The results of a series of measurements at different temperatures are shown in Fig. 4, where the critical magnetic field of each sample is plotted as a function of temperature. The critical temperatures were obtained by extrapolating these curves to zero magnetic field.

In the course of repeating the experiments we found that occasionally a sample would have a curve shape of the type shown in Fig. 3(b). In addition to being very broad, the curve has several peaks. This shape indicates that there were several jumps in susceptibility as a function of magnetic field. Behavior of this type was not the property of a particular sample, but would appear and disappear erratically in a given sample in successive runs. This behavior was traced to the procedure used in cooling the sample to liquid nitrogen temperature and in admitting liquid helium into the flask.

The procedure finally adopted was to place a small amount of liquid nitrogen in the outer shield flask.[15] The system was allowed to stand for an hour, and then small amounts of liquid nitrogen were added over the course of another hour. It was possible to get an accurate idea of the temperature of the samples during cooling by measuring the change in resistance of the copper coils surrounding them; and so bring the samples slowly through the freezing temperature of mercury. We found it important never to permit the initial blow-off of warm helium gas from the transfer tube to hit the samples. We waited until liquid helium poured from the transfer tube before placing the tube into the

[15] The helium Dewar flask had air contained between the walls at a pressure of 1 cm of Hg, permitting heat exchange with the liquid nitrogen. When liquid helium was admitted into the flask the air froze out.

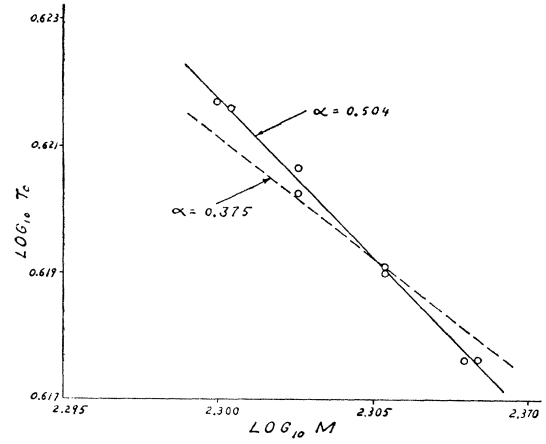

FIG. 5. $\log_{10}$ (critical temperature) *vs* $\log_{10}$ (average mass number).

helium flask. This procedure, which clearly produced the minimum amount of strain in the samples, resulted in consistently good curve shapes.

Omitting the occasional samples which behaved as shown in Fig. 3(b), the "isotope effect" was observed in each of our total of twelve runs on mercury.

Most of these runs were taken in the region 4.0°K to 4.2°K; however, the critical magnetic field measurements were extended down to 1.7°K in two runs. Within experimental error, the critical magnetic fields were found to be parabolic functions of the temperature. The experimental data were fitted to a parabolic relation of the form

$$H=A-BT^2, \tag{1}$$

where T is the absolute temperature. The parameters A and B were determined by the method of least squares.

In Table I we present a summary of what we consider the most reliable values of the transition temperatures of six isotopic samples of various average mass numbers and of the natural metal.

We delay giving the values of the parameters A and B until the next section.

4. DISCUSSION

Figure 5 is a plot of $\log_{10}T_c$ as a function of $\log_{10}M$. The slope of the line is -0.504. For purposes of comparison, a line of slope -0.375 is drawn, according to the suggestion of Herzfeld, Maxwell and Scott.[16] The larger negative slope clearly gives the best fit with the data, and we feel that these experiments firmly establish the relation

$$M^{\frac{1}{2}}T_c=\text{const}$$

in mercury.

Kok[17] has shown that a parabolic relation between critical magnetic field and absolute temperature follows from a specific heat relation of the form

$$C_n-C_s=\gamma T-KT^3,$$

where C_n is the specific heat per unit volume in the normal state, C_s is the specific heat per unit volume in the superconducting state and γ and K are parameters. The first term, γT, is the usual electronic specific term of the free electrons in the normal conductor. From our parameters A and B in Eq. (1), it is therefore possible to calculate γ and K for each isotope; the results are summarized in Table II. The critical fields at 0°K, H_0, obtained from Eq. (1), are also listed.

TABLE II. The critical fields, H_0 at 0°K, and the parameters γ and K, in the specific heat expression, $C_n-C_s=\gamma T-KT^3$, for various average isotopic mass numbers M. K/M is also tabulated.

M	H_0 (oersteds)	γ	K	K/M
199.5	420	1600	273	1.37
200.7	419	1600	275	1.37
202.0	417	1600	278	1.375
203.2	414	1590	278	1.37

It is fairly clear from Table II that γ is independent of M, indicating, as probably was to be expected, that the electronic specific heat in the normal state is unaffected by the mass of the lattice atoms. K, on the other hand, is approximately proportional to the lattice mass.

5. ACKNOWLEDGMENT

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[16] Herzfeld, Maxwell, and Scott, Phys. Rev. **79**, 911 (1950).

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