High Frequency Surface Resistivity of Tin in the Normal and Superconducting States*

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Measurements have been made at a frequency of 9400 megacycles per second of the unloaded Q of a tin cavity from 74.9°K down to 1.26°K. From the value of the unloaded Q and a knowledge of the geometry of the cavity, the high frequency surface resistivity of white tin has been calculated as a function of temperature in both the normal and the superconducting states. In the normal state at low temperatures, the surface resistivity becomes independent of the d.c. resistivity in agreement with workers at other frequencies. In this region the experimental data are compared with the theoretical curves of Sondheimer and Reuter and a value obtained for the number of conduction electrons per atom. Below the superconducting transition temperature the resistivity drops rapidly with temperature, approaching asymptotically a value of 1.9 percent of the value of the resistance at the transition temperature. The results are compared with the data of Pippard and the probable dependence of residual resistance on the method of preparing the tin samples is discussed.

I. INTRODUCTION

THE London model of superconductivity assumes that in the superconducting state the conduction electrons simultaneously exhibit two modes of behavior. A certain superconducting fraction behaves according to the phenomenological equations of F. London and H. London.[1] The rest exhibit the normal resistive behavior. The presence of a steady applied e.m.f. results in the flow of only superconducting electrons with the resulting zero resistance observed experimentally.

In 1934 H. London[2] predicted that high frequency alternating electromagnetic fields would cause the simultaneous flow of normal and superconducting electrons in the surface of the superconductor, the flow of the normal electrons giving rise to a small but finite resistance. This high frequency resistance should reach zero only when all the conduction electrons are in the superconducting state, a condition thought to exist only at absolute zero.

In 1940 H. London[3] experimentally verified the existence of this resistance in superconducting tin at a frequency of 1500 megacycles per second. He measured the Joule heating produced in a tin ellipsoid placed in a high frequency electromagnetic field. The resistance dropped suddenly at the superconducting transition temperature to a small but finite value, decreasing with further decrease in temperature, probably to zero at the absolute zero.

In the same experiment London observed an anomalous behavior in the high frequency surface resistance of non-superconducting tin in the region just above the superconducting transition temperature. The experimental value was much higher than that predicted from direct current conductivity measurements and the classical theory of the skin effect. He concluded that this value of resistance might be due to the long mean free path of the electrons which exceeds the high frequency skin depth at these temperatures.

The present experiment was begun in an effort to extend the work of London to a higher frequency, making use of the improvements in microwave techniques brought about as a result of the war. Measurements have been completed[4] at a frequency of 9400 megacycles per second on the unloaded Q of a Hilger tin cavity from 75°K down to 1.26°K. From the value of the unloaded Q and a knowledge of the geometry of the cavity, the high frequency surface resistance of white tin has been calculated as a function of temperature in both the normal and the superconducting states.

Other postwar investigators[5–9] have extended London's work both experimentally and theoretically. The results of their work will be compared with the results of this experiment in the section on results.

II. METHOD

The measurements at each temperature consisted in determining as a function of frequency near resonance the standing wave ratio looking into a very pure tin cavity. As will be discussed below, these data yield for each temperature three different Q's: Q_u, the unloaded Q of the cavity; Q_L, the loaded Q of the cavity; Q_R, the radiation Q, where

$$Q_u = 2\pi \frac{\text{Energy stored in cavity}}{\text{Energy dissipated in cavity walls per cycle}},$$

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*** Assisted by the ONR.
[1] F. London and H. London, Physica **2**, 341 (1935).
[2] H. London, Nature **133**, 497 (1934).
[3] H. London, Proc. Roy. Soc. **A176**, 522 (1940).
[4] W. M. Fairbank, Phys. Rev. **76**, 167 (1949).
[5] A. B. Pippard, Proc. Roy. Soc. **A191**, 371 (1947).
[6] Bitter, Garrison, Halpern, Maxwell, Slater, and Squire, Phys. Rev. **70**, 97 (1947).
[7] Maxwell, Marcus, and Slater, Phys. Rev. **74**, 1234 (1948).
[8] A. B. Pippard, Nature **162**, 68 (1948).
[9] G. E. H. Reuter and E. H. Sondheimer, Proc. Roy. Soc. **A195**, 336 (1948).

$$Q_L = 2\pi \frac{\text{Energy stored in cavity}}{\text{Energy dissipated in cavity walls} + \text{energy radiated back to line per cycle}},$$

$$Q_R = 2\pi \frac{\text{Energy stored in cavity}}{\text{Energy radiated back to line per cycle}}.$$

The surface resistance is calculated from the unloaded Q, and the consistency of the radiation Q serves as a check on the accuracy of the unloaded Q.

The use of a magic T bridge and a recorder make possible a very rapid measurement of standing wave ratios. The unloaded Q can be measured in a single run on the same cavity throughout the entire range of temperature, even though the Q changes from a value of 6,000 at 75°K to 1,180,000 at the lowest temperature reached.

III. EXPERIMENTAL DETAILS

A block diagram of the apparatus is shown in Fig. 1. Oscillator 1 is a Pound IF stabilized oscillator,[10] stabilized by a wave meter whose frequency can be varied by very small increments. This is accomplished by inserting a fine micrometer controlled probe of diameter 0.045 inches axially into one end of a standard TE_{011} wave meter. A change of 0.0001 inches in the probe depth represents a change in frequency of about 1.5 kc/sec. The change in frequency of oscillator 1 caused by a given change in setting of the reference wave meter can be determined by two methods: (1) The shift in the beat frequency between oscillators 1 and 2 can be measured accurately on the BC-221 frequency meter when oscillator 2 is held at a constant frequency while the frequency of oscillator 1 is varied. (2) Side band signals caused by the superposition of the outputs of the BC-221 frequency meter and oscillator 1 can be observed on the spectrum analyzer. As the frequency of oscillator 1 is varied, the frequency shift can be measured by observing the shift of the side band pattern on the analyzer.

The output of oscillator 1 is fed past a monitor and magic T[11] to one arm of the magic T shown at the lower right hand side of the diagram. This magic T bridge contains the tin cavity on one side arm and a matched load on the other. The output arm contains a detecting crystal C, the output of which is fed to a photo-cell amplifier and then to recorder 1, a Brown recording potentiometer. It is assumed that the energy received by crystal C is proportional to the energy reflected from the cavity.[11] In order to insure that this is true, the magic T bridge containing the cavity has been carefully matched, and three very well matched 3 db attenuator pads have been inserted in the arms of the bridge as shown. Recorder 2 serves to continually

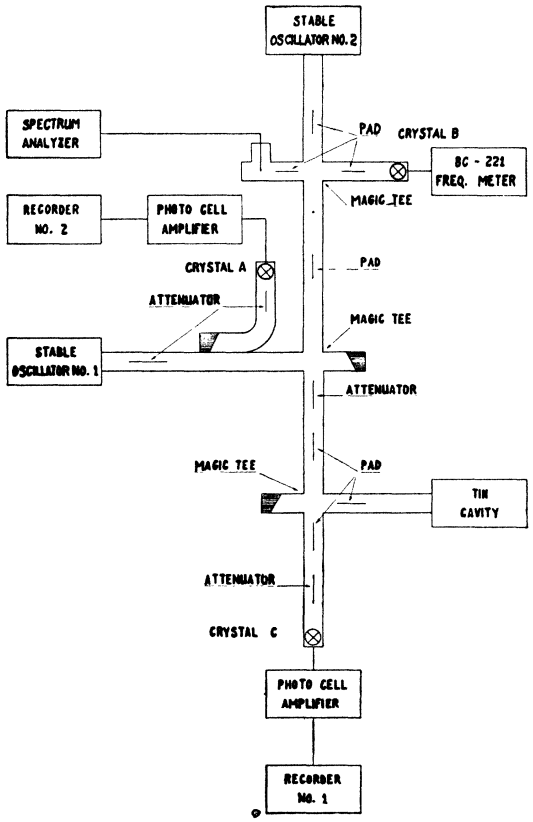

FIG. 1. Block diagram of the apparatus.

monitor the signal incident on the tin cavity. It is connected to a 20 db two-hole directional coupler.

Oscillator 2 is also IF stabilized and serves as a monitor on the frequency of oscillator 1. The beat frequency between the two oscillators can be monitored on the BC-221 frequency meter. The spectrum analyzer serves as a convenient check on the two stabilized oscillators.

A Q measurement is made in the following way. The frequency of the stabilized oscillator is varied in small discontinuous jumps by means of the fine frequency control on the reference wave meter. A signal is recorded on the recorder, the amplitude of which is proportional to the power reflected from the tin cavity. The ratio of this amplitude to the amplitude of the signal reflected far from resonance gives the fraction of power reflected from the cavity at the given frequency. This assumes that the cavity acts as a perfect reflector far from resonance. Account must be taken of the variation in output of the oscillator with frequency. This is done by use of the recorder 2 which serves as a monitor, or by extrapolation from the signal received far from resonance on each side of the Q curve. Subject to this correction, one thus obtains on the recorder the percent power reflected from the cavity as a function of frequency. This yields directly the standing wave ratio, and hence Q_R, Q_u, and Q_L.

[10] R. V. Pound, Rev. Sci. Inst. **17**, 490 (1946).
[11] C. G. Montgomery, *Technique of Microwave Measurements*, (McGraw-Hill Book Company, Inc., New York, 1948), Radiation Laboratory Series, Vol. 11.

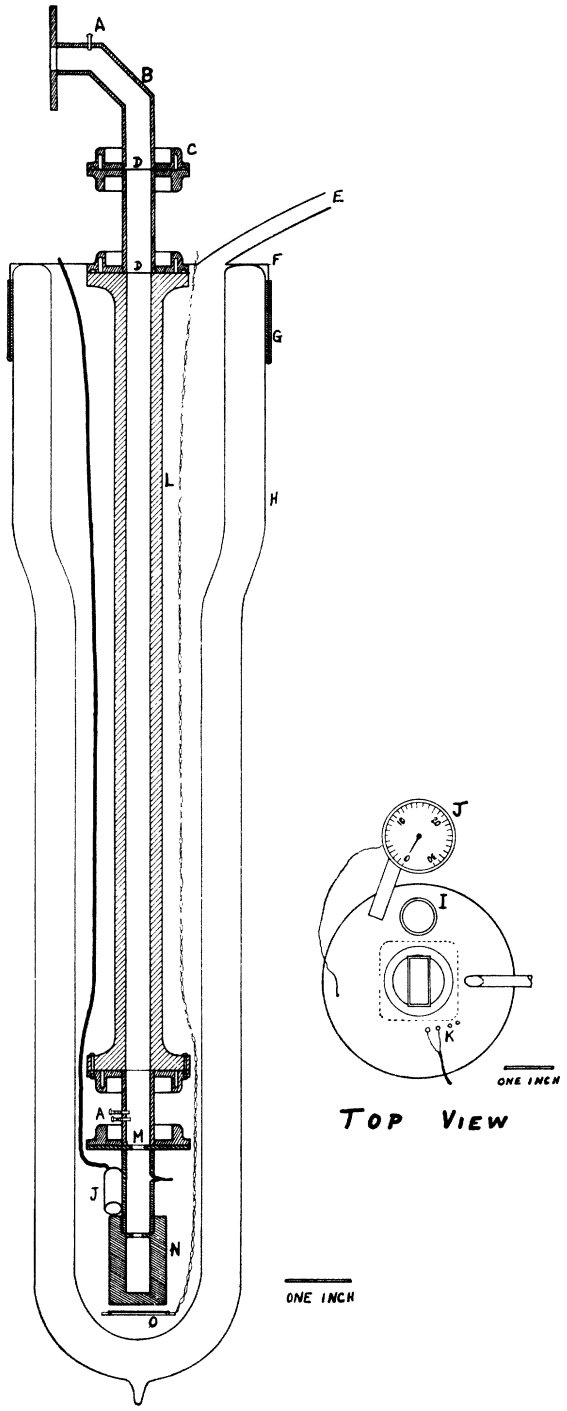

FIG. 2. Section view of the helium Dewar assembly. *A*—matching screw, *B*—brass wave guide, *C*—choke flange coupling, *D*—mica seal, *E*—exit tube (also used for manometer line), *F*—metal top, *G*—rubber gasket, *H*—helium dewar, *I*—inlet tube (also used for pumping line), *J*—constant volume helium thermometer, *K*—metal to glass connectors, *L*—silvered glass wave guide, *M*—resonant glass window, *N*—tin cavity, *O*—heater.

The tin sample measured consisted of a rectangular cavity 0.400 inches high by 0.898 inches wide by 0.882 inches long, coupled to the wave guide by a hole approximately 0.170 inches in diameter. The cavity was the same cross section as the coupling wave guide and was electrically one-half wave-length long. This type of cavity was used since the radiation Q of such a cavity is independent of the unloaded Q. It also offers advantages in ease of assembly. The cavity was made from spectroscopically pure tin supplied by Johnson, Matthey and Company of London, the purity being 99.992 percent.

In an attempt to obtain a very smooth uncontaminated surface, the cavity was pressed out with a die. The die was formed from tool steel, hardened, and polished to a mirror finish with a rouge lapping wheel. The cavity was cut along the center line in the wide side of the guide, the die completely forming each half. No currents flow across this particular plane, hence no loss should be caused by poor contact at this point. The two halves of the cavity were sealed with eutectic solder in a hydrogen oven and coupled to the external wave guide through a resonant glass window of the type used in making TB boxes for radar sets.[12] The final cavity was evacuated and sealed tight.

Figure 2 shows a section view of the helium Dewar and assembled apparatus. The cavity was connected to the top of the Dewar by means of a rectangular glass wave guide to minimize heat leak. With the glass wave guide it was possible to keep helium for as long as eight hours, and to make measurements at temperatures above 4.2°K as will be described below. The guide was formed from thick round glass tube by a series of tapered graphite dies inserted when the glass was molten. Flange ends had been welded on to the glass tube before the die was inserted. The inside of the glass wave guide was made slightly undersize and then ground and polished to size. The wave guide was silvered on the inside by chemical deposition. The other microwave plumbing shown in Fig. 2 was made from the standard rectangular wave guide, coupled by the usual choke flange coupling.

In order to avoid any possibility of the formation of grey tin on the surface of the cavity, the cavity was cooled down very rapidly to nitrogen temperature and warmed up rapidly from this point when a run had been completed. The temperature in the helium region was determined by vapor pressure measurements making use of the 1937 Leiden temperature scale. Heat was supplied by heater 0 at the bottom of the flask when raising the temperature in the helium I region. This insured temperature equilibrium during the process.

To obtain Q measurements in the region above 4.2°K, the following technique was used. When the liquid helium had completely evaporated from the flask, the flask was evacuated and allowed to warm up very slowly toward the temperature of the surrounding nitrogen jacketing flask. The cavity, insulated by the

[12] M. D. Fiske, Rev. Sci. Inst. **17**, 478 (1946).

vacuum and glass wave guide, took several hours to warm up, and it was possible to measure Q curves at several intermediate points between liquid helium and liquid nitrogen temperatures. The temperature of the cavity was determined by the constant volume helium thermometer shown as J in Fig. 2.

IV. CALCULATION OF Q

As can be seen from the definitions given previously,

$$1/Q_L=1/Q_R+1/Q_u.$$

If we define r_0 as the voltage standing wave ratio looking into the cavity at resonance, then it can be shown[11,13] that

$Q_u=(1+r_0)\times Q_L$ and $Q_R=Q_u/r_0$ for overcoupled cavity,

and

$Q_u=(1+1/r_0)\times Q_L$ and $Q_R=Q_u\times r_0$ for undercoupled cavity. The width of the resonance curve determines Q_L. Q_u and Q_R can also be determined if r_0 is known.

As has been pointed out above, one can calculate from the data on the recorder the standing wave ratio r looking into the tin cavity as a function of frequency near resonance. The equation for the resonance curve can be put in a very convenient form to make maximum use of the data.[13] This form of the equation for the resonance curve is:

$$(2\Delta Q_u G/Y_0)^2(Y_0/G)+Y_0/G+G/Y_0=(1+r^2)/r$$

where ω_0 = frequency at resonance, r = voltage standing wave ratio at frequency ω, Y = line admittance, $\Delta=(\omega-\omega_0)/\omega_0$, and G = input conductance to the cavity.

If the cavity is undercoupled, $Y_0/G=1/r_0$, and if overcoupled, $Y_0/G=r_0$. Thus, the equation of the resonance curve is, for the undercoupled case,

$$4Q_u^2r_0\Delta^2+(1+r_0^2)/r_0=(1+r^2)/r,$$

and for the overcoupled case

$$(4Q_u^2/r_0)\Delta^2+(1+r_0^2)/r_0=(1+r^2)/r.$$

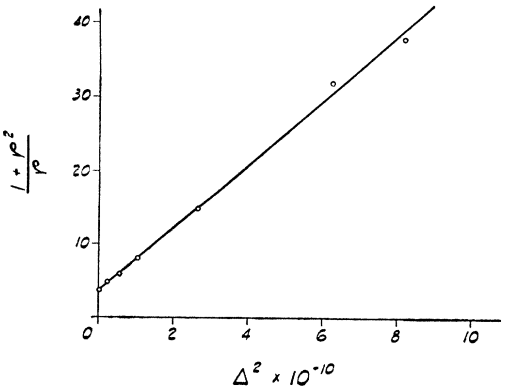

FIG. 3. Sample of straight line graph used to determine Q_u and Q_R.

[13] E. Maxwell, J. App. Phys. **18**, 629 (1947).

These two equations are equations of straight lines with intercepts at $(1+r_0^2)/r_0$, and with slopes $4Q_u^2r_0$ for the undercoupled case and $(4Q_u^2/r_0)$ for the overcoupled case. Thus, if Δ^2 is plotted against $(1+r^2)/r$, both Q_u and r_0 can be calculated from the slope and intercept of the curve. Q_R can be calculated from r_0 and Q_u by the formulas given above.

Figure 3 is a sample of a graph of $(1+r^2)/r$ plotted as ordinate against Δ^2 as abscissa. The self-consistency of the data can be checked by observing whether or not the above curve is a straight line, and whether or not Q_R is constant for all values of Q_u.

V. RESULTS

The unloaded Q of the tin cavity described above increased from 6060 at 74.9°K to an almost constant value of 23,000 as the temperature was lowered to 3.722°K. Below this temperature Q_u increased rapidly, reaching a value of 1,180,000 at 1.26°K, the lowest temperature reached. The 1937 temperature scale was used in evaluating the data. For all values of Q_u, Q_R remained constant at 190,000 to within an average deviation of 3 percent. This serves as a check on the accuracy of Q_u.

The experimental data can be divided into two parts, that obtained above the superconducting transition temperature of 3.722°K, and that obtained below this temperature. The former will be considered first.

In order to compare the data with those of other workers in the field, the surface resistivity, R, has been calculated from the unloaded Q and a knowledge of the geometry of the cavity.[5,11,14] For the cavity used, $R=1/0.00505Q_u$. A plot of $1/R$ against the $\sigma^{\frac{1}{2}}$, where σ is the d.c. conductivity, should result in a straight line as long as the classical expression for the skin depth holds. The data obtained above 4.2° are plotted in this fashion in Fig. 4.

The d.c. conductivity was calculated using the data of Onnes and Tuyn,[15] assuming the conductivity at

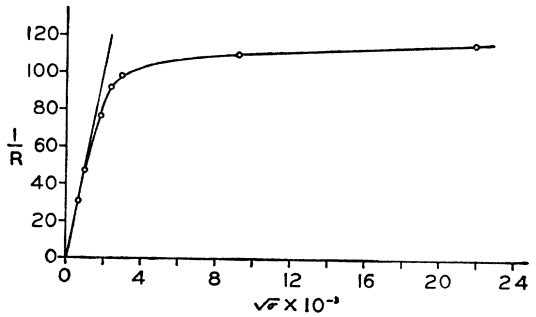

FIG. 4. A plot of the data above the superconducting transition temperature. $1/R$ is calculated from Q_u and σ is the d.c. conductivity. The straight line is the theoretical curve under the assumption that the classical expression for the skin depth holds.

[14] S. A. Schelkunoff, *Electromagnetic Waves* (D. van Nostrand Company, Inc., New York, 1943).

[15] H. Kammerlingh Onnes and Tuyn, Int. Crit. Tab. **6**, 124 (1929).

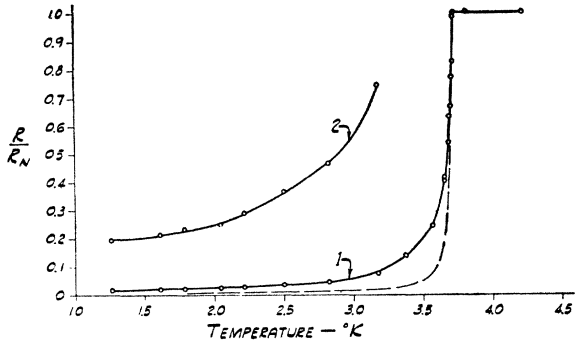

FIG. 5. Graph of the data below the superconducting transition temperature of 3.722°K. R_n is the surface resistivity at the transition temperature. The dotted line indicates the results of Pippard taken at the lower frequency of 1200 megacycles per second. For clarity, R/R_N has been multiplied by 10 and plotted in curve 2.

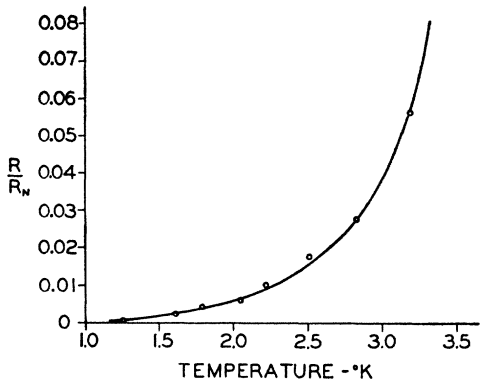

FIG. 6. The solid curve is a graph of the equation $r=0.0865\times[t^4(1-t^2)/(1-t^4)^2]$, where $t\equiv T/T_c$, given by Pippard as an empirical equation representing below 3.3°K his data on tin at 9200 megacycles per second. The circles represent the data of the present experiment after the residual resistivity, $R=0.019R_n$, has been subtracted from the original data.

4.2°K to be 4.8×10^8 ohm^{-1} cm^{-1} as obtained by Pippard[4] for a sample of Johnson Matthey tin of similar purity. The validity of Matthiessen's rule was assumed.

An inspection of Fig. 4 reveals that $1/R$ becomes almost independent of the d.c. conductivity for low temperatures (high σ). At a lower frequency of 1200 megacycles per second, Pippard[5] has observed the same effect for several metals including tin. He has proposed a theoretical explanation based on the long mean free path of the electrons which at low temperatures exceeds the penetration depth of the high frequency electromagnetic fields. Maxwell, Marcus, and Slater[7] and Nowak and Slater[16] have studied the same effect in tin at 24,000 megacycles per second.

Reuter and Sondheimer,[9] using the modern theory of metals, have given a rigorous extension of Pippard's theory. For the microwave region they have plotted two theoretical curves, one assuming perfectly specular reflection of electrons from the surface of the metal ($p=1$), the other assuming completely diffuse reflection ($p=0$). Instead of plotting $1/R$ against $\sigma^{\frac{1}{2}}$ as done in Fig. 4 for the experimental data, they have plotted A/R against $\alpha^{1/6}$ where A is a normalizing factor and $\alpha^{1/6}$ where A is a normalizing factor and $\alpha^{1/6}$ is proportional to $\sigma^{\frac{1}{2}}$.

$$A=6^{\frac{1}{2}}(\pi\omega/\epsilon c^2)^{\frac{1}{2}}(h^3/72\pi n^2)^{1/9}$$

(obtained from combining Eqs. (20) and (51) in reference 9),

$$\alpha=\frac{3^{5/3}\pi^{1/3}\omega\sigma^3h^2}{8^{2/3}c^2\epsilon^4n^{4/3}}$$

(obtained from combining Eqs. (8), (19), (20) of reference 9), where ω = angular frequency of the electromagnetic waves, h = Planck's constant, c = velocity of light, ϵ = electronic charge, n = number of conduction electrons per cubic centimeter of tin. Electrical quantities are expressed in Gaussian units.

[16] W. B. Nowak and J. C. Slater, Phys. Rev. **76**, 469 (1949).

Since both A and $\alpha^{1/6}$ are proportional to $n^{-2/9}$, a value for n can be obtained by adjusting A to give an approximate fit between experimental and theoretical curves. The exact value obtained for n depends upon the type of reflection assumed at the surface of the tin. If diffuse reflection is assumed and the experimental data of this experiment are fitted to the lower theoretical curve ($p=0$), a value of 7.3×10^{21} conduction electrons per cc or 0.20 conduction electrons per atom is obtained. If specular reflection is assumed and the data are fitted to the upper theoretical curve ($p=1$), a value of $n=4.3\times10^{21}$ conduction electrons per cc or 0.12 conduction electrons per atom is obtained. Pippard's data yield a median value of 0.87 conduction electrons per tin atom,[9] while Maxwell, Marcus and Slater[17] have obtained values of 0.12 and 0.20 assuming, respectively $p=1$, and $p=0$.

The second part of the experiment involves the resistivity R in the superconducting region below $T_c=3.722$°K. R_N is the resistivity at T_c. Figure 5 is a plot of $r\equiv R/R_N$ against temperature. Also plotted on the same graph is a dotted line representing the data of Pippard taken at a frequency of 1200 megacycles per second. Pippard's data have been shifted to the 1937 temperature scale. The transition temperatures are 3.725°K in Pippard's experiment and 3.722°K in this experiment. For any given temperature, r increases with increase in frequency.

Subsequent to his work at 1200 megacycles per second, Pippard performed experiments on tin at 9200 megacycles per second.[8] These were conducted concurrently with the experimental work of this paper and permit comparison of the effect of different methods of preparing the tin specimen.[18] Pippard states that his

[17] Maxwell, Marcus, and Slater, paper submitted to the Physical Review.

[18] In a private communication, Pippard has discussed the two experiments and states that his specimens are $\frac{1}{2}$ wave resonant wires prepared by drawing molten tin into thin-walled glass tubes

results in these experiments can be represented for $T_c<3.3°K$ by the empirical equation

$$r=A'[t^4(1-t^2)/(1-t^4)^2],$$

where $t\equiv T/T_c$ and $A'=0.0865$. The curve in Fig 6. is a graph of this empirical equation with r plotted against T.

Extrapolation of the experimental data of this paper (Fig. 5) to absolute zero gives a residual value of $r=0.019$. The circles in Fig. 6 represent the data of the present experiment after the residual value of R has been subtracted from the original data. It is seen that, after this subtraction is made, the data of the present experiment at 9400 megacycles per second agree with Pippard's data at 9200 megacycles per second.

London has assumed that all of the electrons become superconducting at the absolute zero, and that therefore the limiting value of $r=R/R_N$ at this temperature should be zero. The tin specimens used by Pippard were cast into wires which were mounted by means of low loss dielectric supports. In order to determine r for very low temperatures it was necessary to subtract out the loss due to the dielectric supports. After subtracting out this dielectric loss, Pippard found at 1200 megacycles per second that r apparently does extrapolate to zero for mercury but not for tin, although the dielectric loss is difficult to calculate with certainty. At 9200 megacycles per second, Pippard's results for tin apparently do extrapolate to zero after accounting for the dielectric loss.[18] In the present experiments and in the experiments by Maxwell, Marcus, and Slater,[7] the tin was pressed into a rectangular cavity requiring no dielectric material in the cavity. As mentioned above, an apparently constant residual resistance of $r=0.019$ was found in the present experiment. A residual resistance of 0.09 was found by Maxwell, Marcus, and Slater at 24,000 megacycles per second.[17]

In any experiment of this kind, one of the most difficult experimental problems is to prepare surfaces which behave exactly as the bulk metal. Electrically the cavity used in this experiment operates in a single mode, and the resistivity R can be calculated from the Q_u and the dimensions of the cavity. Q_R remains constant for all values of Q_u and serves as a check on the validity of each measurement of Q_u. Great care was taken in making the die and pressing out the cavity. The cavity was soldered under vacuum and carefully annealed. The presence of a residual resistivity of 1.9 percent of R_N found in this type of cavity and apparently lacking in the cast specimens used by Pippard at 9200 megacycles per second, seems to indicate that a pressed surface acts less like the bulk metal than a cast surface. Unless some new frequency effect is appearing at 24,000 megacycles per second, the residual resistance found in the pressed cavities of Maxwell, Marcus, and Slater indicates the same effect.

The data in the normal state also seem to indicate a more ideal surface for the cast specimens than for the pressed specimens. According to the theory of Sondheimer and Reuter,[9] R_N should vary with frequency as $\omega^{\frac{1}{3}}$. A frequency variation of $\omega^{0.86}$ is found when R_N in this experiment is compared with R_N found by Pippard at 1200 megacycles per second, while Pippard has quoted a variation of $\omega^{\frac{1}{3}}$ in comparing his two experiments with cast specimens.[18] It was observed above that n, the number of superconducting electrons per tin atom, was larger when calculated from Pippard's data at 1200 megacycles per second than when calculated from the data of this experiment or the experiment of Maxwell, Marcus, and Slater. This may give further indication of the same effect.

It has been shown that, when the superconducting residual resistance found in this experiment is subtracted from the experimental values of R and R_N, the value of $r\equiv R/R_N$ is in close agreement with the data of Pippard at 9200 megacycles per second. It appears probable either that some constant loss which has not been accounted for exists in the cavity used in this experiment or that part of the surface penetrated by the electromagnetic field, of the order of 1.9 percent, remained non-superconducting after being subjected to the pressing process. The formation of grey tin would give this effect, but as has been pointed out above, great care was taken to avoid this transformation.

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under vacuum, the glass being later removed. The method of preparing the sample constitutes the main difference in the two experiments.