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# SOME EXPERIMENTS AT RADIO FREQUENCIES ON SUPERCONDUCTORS

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### ABSTRACT

Measurements were made in the temperature range 2.5 to  $4.2^{\circ}$  K on wires of tin and of tantalum. A tin wire in the superconducting transition range carrying an alternating current of frequency 200,000 c/s (cycles per second) superposed on a direct current was found to exhibit a potential drop having a strong component of double the applied frequency. This indicates that the superconducting state can be destroyed by a magnetic field and re-created in a time interval of less than  $10^{-6}$  sec. For each substance the transition temperature from the normal resisting to the superconducting state was found to be the same for alternating currents of radio frequency as for direct currents. The effective resistance of the specimens when below their transition temperatures was found to be too small to detect at radio frequencies by the calorimetric and electrical methods tried (i. e., less than 4 percent of that above the transition temperature in the case of tin and less than 1 percent in the case of tantalum).

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## I. INTRODUCTION

Since our communication in  $1931^{1}$  reporting on some experiments on the superconductivity of tin for alternating currents, we have carried on intermittently, as other work permitted, a series of experiments comparing for alternating and for direct currents the performances of the superconductors tin and tantalum in the form of solid wires. Three different phases of the problem were investigated: (1) the time required for the establishment and for the destruction of the superconducting state by changes in the magnetic field; (2) the relation between the temperatures at which the superconducting transition occurs for high-frequency current and for direct current; and (3) the resistance to the flow of high-frequency currents at temperatures below the transition.

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<sup>1</sup> Silsbee, Scott, Cook, and Brickwedde. Phys. Rev. 39, 379 (1932).

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The tin specimens were made from NBS Standard Sample material, 99.99 percent pure, which was extruded at an elevated temperature into wire 0.022 cm in diameter. The tantalum wire, 0.0075 cm diameter, was in the hard-drawn condition as purchased from the Fansteel Co. Spectrochemical analysis of the tantalum showed only small amounts of Sn and Si (not over a few tenths percent) and traces of Fe, Ca, Al, and Cb. This tantalum showed an abnormally high resistance (0.26 times its resistance at 0° C) at 4.0° K and a low transition temperature, 3.94° K, as compared with 4.4° K for the tantalum reported by Meissner.<sup>2</sup> The variation of the critical magnetic field with temperature  $(dH_c/dT)$  was 150 oersteds <sup>3</sup> per degree for the tin and 1,250 oersteds per degree for the tantalum. This high value of  $dH_c/dT$  for tantalum and its comparatively large  $R/R_0$  at low temperatures would class our specimen, like many alloys, in the category of anomalous superconductors. It was also found, as seems to be a characteristic of alloys, that the magnetic field produced at the surface of the wire by the critical current is much smaller than the critical value of an externally applied magnetic field, the magnetic field of the critical current for the alloy being of the same order as the critical magnetic field for pure metals. The magnetic field of the critical current was found to increase at a rate of only 50 oersteds per degree as the temperature was decreased.

The specimens were formed by winding the wire bifilarly on glass or paper forms, and were provided with current and potential terminals at both ends. The d-c resistances of the two tin and one tantalum specimens, on which most of the data were obtained, were 65, 15, and 95 ohms, respectively, at room temperature, and 0.06, 0.012, and 25 ohms, respectively, at 4.0° K. For small currents, the transition temperatures were 3.738 and 3.961° K for the tin and tantalum specimens, respectively. The temperature at which the resistivity of a specimen is half its value in the normal resisting state was taken as its transition temperature. Temperatures were calculated from the observed vapor pressures of the liquid-helium bath in which the specimens were immersed, using the vapor-pressure equation reported by Keesom, Weber, and Norgaard.<sup>4</sup> In the range of temperatures of this investigation, a change in temperature of 0.001° K corresponds to a change in the vapor pressure of helium of about 0.5 mm of Hg.

## II. TIME REOUIRED FOR THE ESTABLISHMENT AND DESTRUCTION OF THE SUPERCONDUCTING STATE

The fact that a conductor in the superconducting state offers no measurable resistance to a high-frequency alternating current affords no direct evidence that the times required for the establishment and destruction of the superconducting state are short. With the aid of high-frequency currents, however, it is possible to investigate this question.

Suppose a specimen is subjected to a rapidly pulsating magnetic field, such as might be produced by the superposition of a direct and an alternating component; suppose the magnitudes are such that at

<sup>&</sup>lt;sup>2</sup> Z. Physik 61, 191 (1930).

 <sup>&</sup>lt;sup>2</sup> D. Physik 61, 191 (1930).
 <sup>3</sup> In accordance with the formal action of the International Electrotechnical Commission in 1930 and of the International Union of Pure and Applied Physics in 1932, we here use the name "corsted" for the cgs unit of magnetic-field intensity in place of the name "gauss," which is still frequently used for both this unit and that of magnetic-flux density.
 <sup>4</sup> Keesom, Weber, and Norgaard. Leiden Communication 202b (1929).

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sustained values of the field equal to the maxima, the specimen has normal resistance; but suppose the temperature is such that in the continued absence of the field, the specimen is superconducting. If, now, the time required for the establishment or for the destruction of the superconducting state is long as compared with the period of the pulsations, the specimen would be expected to have a nearly constant resistance. If the times required are short, the specimen would oscillate between the superconducting and normal resisting conditions with each cycle of the pulsation. Let, now, a single-frequency alternating current, synchronous and in phase with the alternating component of the magnetic field, be sent through the specimen. If then, the times required for the establishment and destruction of the superconducting state are short, the wave form of the (IR) potential drop across the specimen will differ from the simple sine-form of the current and have a strong double-frequency component. Such a distortion of wave form would not be expected if the time required for the establishment or the destruction of the superconducting state were long as compared with the period of the pulsations.

The requisite conditions were met most simply by superposing direct and alternating currents of appropriate values in a wire of circular cross section. For any particular value of the direct current there is a range of temperatures in which the magnetic field of the direct current at the surface of the wire is only slightly less than the magnetic field of the critical current for the specimen. If a sufficient alternating current is superposed, then during most of one-half of the cycle when the fields are aiding, the total field in the outer regions of the wire exceeds the critical value and, if the material can follow the pulsations, it has resistance. During the other half of the cycle, when the fields are opposing, the total field is less than the critical value and the resistance is zero. The potential difference at the terminals of a wire having such a cyclically varying resistance and being traversed by a single-frequency alternating current would be expected to have a component of double the fundamental frequency. It may be noted that by reason of the skin effect the high-frequency current is confined to the outer regions of the wire.

A double-frequency component originating in the way described can be distinguished from spurious effects, such as harmonics in the current source, by the following criteria: (1) When the temperature is so low that the magnetic field is less than the critical magnetic field, even at that crest of the a-c wave which adds to the direct current, the expected double-frequency component should be absent; (2) when as a result of either (a) high temperature or (b) high direct current, the magnetic field is greater than the critical magnetic field even at the crest of the a-c wave that is opposed to the direct current, the double-frequency component should be absent; and (3) when the direct current is zero, and the crest value of the magnetic field of the alternating current exceeds the critical value, the wave form of the (IR)-potential drop, while distorted, should be symmetrical and, hence, contain only odd harmonics so that the double-frequency component would not be observed.

The experimental arrangement shown in figure 1 was used. Specimen S was supplied with direct current from battery B through ammeter  $A_0$  and adjustable rheostat  $R_0$ . The d-c potential across the

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ends of the specimen was measured by the deflection of the galvanometer  $G_0$ , which was connected to the potential leads at the ends of the specimen. This galvanometer,  $G_0$ , was calibrated with a potentiometer not shown in the figure. The radio-frequency oscillator was coupled magnetically with coil  $L_1$ , and induced the main alternating current through the circuit  $L_1R_1A_1SC_1$ . The detecting circuit  $L_2C_2S$ was connected to the potential leads and tuned to double the oscillator frequency. To still further reduce the fundamental current flowing in  $L_2C_2$ , the auxiliary circuit L'C'R'M, tuned to the oscillator frequency, was provided and so adjusted as to insert at M an emf



FIGURE 1.—Circuits used to detect pulsation in resistance.

S, tin specimen; B, battery supplying d-c component of current;  $L_1R_1A_1C_1$ , tuned circuit supplying a c component of current;  $L_2C_2$ , detecting circuit tuned to double frequency; L'C'R'A', circuit compensating fundamental frequency; and D, crystal detector.

opposed as closely as possible in magnitude and phase to the fundamental component of the potential drop in the specimen. The crystal detector D, with galvanometer  $G_2$ , indicates the potential drop in coil  $L_2$ . To correlate this with the double-frequency component of potential drop in S, the detector was calibrated roughly by adjusting the oscillator to give double frequency and noting the deflection for known values of M and of current in A', the main circuit through  $L_1C_1$  being opened.

With these circuits, observations were made at 200 and 290 kc/s on the 65-ohm tin specimen. The procedure for any one measurement was to hold the temperature as constant as possible, and for given values of direct and alternating current, as read by milliammeters  $A_0$ and  $A_1$ , respectively, to tune circuit  $L_2C_2$  by adjustment of condenser  $C_2$  until a maximum deflection of  $G_2$  was obtained. This reading was recorded and also the readings when  $C_2$  was thrown off on each side Silsbee, Brickwedde,] Scott

sufficiently to destroy the tuning and yield a reading which was almost independent of the setting of  $C_2$ . This false zero arose, presumably, from lack of perfect neutralization of the fundamental component of the drop by the auxiliary emf of M.



Figure 2 gives the results of a typical set of measurements made at a succession of different temperatures held constant during each measurement, the superposed direct and alternating currents being the same for the entire set. The values plotted in figure 2 are for a run in which the direct current was 69 ma, and the root-mean-square value of the alternating current 143 ma and its frequency 200 kc/s.

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The ordinates of curve I are the deflections of the galvanometer in series with the crystal detector after subtraction of the residual detuned deflection. Curve II is the d-c resistance transition curve derived from the simultaneous deflections of the galvanometer connected across the ends of the specimen through a choke coil.

It is seen from curve I that a small amount of double-frequency component is present at all temperatures, perhaps because of a harmonic in the oscillator, but that a very marked increase in this component occurs in a temperature range at the colder end of the transition range. The small curves at the bottom of figure 2 indicate approximately, for temperatures 3.68, 3.70, and 3.72° K, respectively, the cyclic variation in resistivity (plotted as ordinate) of the outer-most portion of the specimen which would be expected to result at each temperature from the cyclic variation in the total instantaneous current (plotted as abscissa) and hence in the net magnetic field at the surface of the wire. The center of oscillation of the a-c component of the magnetic field is displaced from the origin by the d-c component. In the calculation of the ordinates (resistivity of the surface layer of the wire) of these lower curves, use was made of the resistance transition curve II and its displacement with current (from figure 5 below). If the relations between resistivity and current shown by these curves are combined with the sinusoidal variation of current with time, the resulting variation of resistivity with time shows a fundamental component of the cyclic variation, which is much greater at 3.70° K than at either the higher or lower temperature. The double-frequency component of voltage drop is proportional to this fundamental component in the variation of resistivity. Hence it appears that the observed effect occurs at just the temperature to be expected if the times required to establish and destroy the superconducting state are short, and satisfies the criteria 1 and 2a given above for distinguishing from a spurious effect, a double-frequency component arising in the way expected.

Figure 3 gives the results of a set of measurements taken with the specimen at a constant temperature (3.706°K) and a fixed alternating current of 102 ma (rms), various values of superposed direct current up to 170 ma being used. As before, ordinates are deflections of the galvanometer in series with the crystal detector after subtraction of the residual detuned deflection. In accordance with criterion 3, the double-frequency component is very small when the direct current is zero. It increases to a maximum (at 118 ma) with increasing current and then decreases with further increase of current. The small curves at the bottom of figure 3 show the cyclic variation to be expected in the resistivity of the surface layer of the wire for superposed direct currents of 50, 120, and 170 ma, respectively. Here, as in the case of figure 2, the amplitudes of the variations in resistivity are at least roughly consistent with the observed variation of the double-frequency component (upper curve), if it is assumed that the resistivity follows with practically no lag the variations in current and magnetic field.

A quantitative check based on the magnitude of the doublefrequency component is rendered difficult both by the complexity introduced by skin effect and the experimental difficulty of avoiding stray coupling while calibrating the detector by the emf induced in

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the mutual inductance M, (figure 1.) Of the 12 sets of measurements made at successively different temperatures while the currents were held constant, 8 were secured with reasonably good calibrations. All eight sets corresponded to fairly large current values, so that at the optimum temperature the resistivity of the surface layer should have been carried from zero to full value during each cycle. Taking the current through the detector (and the galvanometer deflections) as proportional to the square of the emf across the detector, the doublefrequency emf induced by the specimen was found to be proportional to the magnitude of the fundamental-frequency current flowing







through the specimen, their ratio being  $0.08 \pm 0.008$  mv/ma. An exact calculation of the magnitude of the double-frequency emf to be expected is not feasible but an approximate calculation shows that with the optimum value of direct current, the double-frequency emf (rms) should be of the order of  $I_1R_1/\sqrt{8}$ , where  $I_1$  is the current (rms) of fundamental frequency and  $R_1$  is the effective a-c resistance of the specimen for this frequency. The effective resistance of the specimen for 200 kc/s was about 0.36 ohm, from which one would expect a double-frequency effect amounting to  $0.36/\sqrt{8}$  equal to 0.13 mv/ma. This is of the same order of magnitude as that observed. The difference in value is no greater than can be attributed to the uncertainties either in experiment or in theory.

We conclude, that if any time at all is required for the establishment and for the destruction of the superconducting state it is short compared with  $5 \times 10^{-6}$  sec and is probably less than  $1 \times 10^{-6}$  sec.

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# **III. TRANSITION TEMPERATURE**

The transition from the normal resisting to the superconducting state of the polycrystalline specimens here used, while occurring within a narrow temperature range, occupied a finite interval of about  $0.02^{\circ}$  K in tin and  $0.05^{\circ}$  K in tantalum. The obvious procedure for determining whether there is a difference between the transition temperatures for direct and high-frequency currents is to observe the resistance of the specimen at various temperatures through the transition range using (a) direct current and (b) radio-frequency current, and to compare the temperatures at which a given fraction (say, one-half) of the resistivity was present. In the case of direct current, the resistance was easily obtained by the usual method of passing a small current, I, measured with a milliammeter, through the current terminals of the specimen and noting the potential difference E, thereby produced between the potential terminals.

A Wenner potentiometer was used sometimes for this latter purpose, but it usually sufficed to leave the dials set on zero, and to note the deflections of the galvanometer, which thus (with suitable shunt and series resistances) served as a voltmeter. The resistance was taken as E/I.

At radio frequencies, however, the matter is not so simple, since ordinary methods of resistance measurement give only the total resistance of the circuit, which was many times that of the tin specimen even when above its transition. The procedure used in most of the measurements was to connect the current terminals of the specimen in series with a thermal milliammeter, an inductance, and an adjustable air condenser. This circuit was then loosely coupled to a simple laboratory oscillator, which used a 210 tube with a plate voltage of 400. The frequency could be adjusted to any desired value from 50 to 4,000 kc/s. The specimen circuit was tuned to resonance, as shown by a maximum of current. The temperature of the cryostat was then allowed to drift slowly through the transition range, while the electrical circuits were left undisturbed. Simultaneous readings of the milliameter and of the vapor-pressure manometer were taken during the change. Transition curves, such as shown in fig. 4, could be plotted from these data, using also the change in current observed when a known resistance was added, and the assumption that the specimen had zero resistance at the cold end of the transition range.<sup>5</sup>

The frequency which could be used effectively was limited to about 1,000 kc/s with the tin specimens and to 3,500 kc/s with the tantalum specimen, because of the unavoidable capacitance of the specimen and its leads to the metallic walls of the liquefier. It is probable that the apparent resistance of the specimen was considerably enhanced by such capacitance effects even below these limits, but the procedure of plotting the transition curves on a percentage basis prevents any such error from appreciably affecting the curves.

A more serious difficulty arose from the lag of the temperature of the specimen behind that of the helium bath in which it was immersed. This was largely avoided by taking the mean of pairs of transitions, one heating and the other cooling. Slight differences in the rate at which the temperature drifted in the two transitions of each pair are probably the main cause of the scattering shown in the results.

<sup>&</sup>lt;sup>5</sup> For details of the resistance variation method, see NBS Circular C74, p. 180 (1924).

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A further complication arises from the magnetic and thermal effects of the current used in making the measurement. The maximum currents used (200 ma for the tin specimens and 30 ma for the tantalum specimen) would be expected to depress the transition by 0.029 and 0.032° K, respectively. The specimens were wound bifilarly but with rather close spacing, so that the mutual action of neighboring





I. Alternating-current resistance as a fraction of the a-c resistance above the transition. II. Alternating-current resistivity as a fraction of the a-c resistivity above the transition. III. Direct-current resistance and d-c resistivity as fractions of their values above the transition.

wires may have appreciably increased the effect as estimated above for a straight wire. A heating effect of the current, while absent at the cold end of the transition, might be present at the hot end. In the case of the tin wire, the great skin effect would make such heating more pronounced at the higher frequencies and might introduce an apparent shift in transition temperature with frequency. Because of the smaller diameter and much larger resistivity of the tantalum specimen, the skin effect in it was negligible.

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To minimize these effects in the final comparison, the data on the two tin samples were plotted as shown in figure 5, in which the ordinates are the temperature of the helium bath at which the specimen showed one-half of its normal resistivity, while the abscissas are the values of the measuring current. The different markings of the points correspond to different frequencies and specimens. It is to be noted that by reason of the great skin effect the attainment of half of normal resistivity corresponds to the attainment of 70.7 percent of the full effective resistance at the radio frequencies used. Although the resist-



FIGURE 5.—Transition temperatures of tin specimens as a function of current.

ance would be expected to first appear as the crest of each wave of alternating current carried the surface material above the critical magnetic field for the existing temperature, it would again drop to zero during much of the cycle, hence, root-mean-square values of the currents rather than crest values were arbitrarily chosen for use as abscissas in figure 5.

The straight lines shown were located by the method of least squares to most nearly fit the data on direct current and on alternating current, respectively. Points at all frequencies other than zero were taken as of equal weight. The intercepts of the two lines are the best available indication of the midpoint of the transition when magnetic and heating effects of the currents are eliminated. These values are  $3.738^{\circ}$  K for direct current and  $3.740^{\circ}$  K for alternating current. The difference,  $0.002^{\circ}$  K, somewhat exceeds the mean-square deviation, which is  $0.0007^{\circ}$  K for either intercept, but is probably not significant.

The slope of the direct current curve,  $2.0 \times 10^{-4}$  °K/ma, is somewhat larger than the value  $1.2 \times 10^{-4}$ , calculated from Tuyn's <sup>6</sup> data, for the case of a single straight wire, presumably because of the mutual magnetic effects of adjacent wires.

<sup>6</sup>J. Franklin Inst. 201, 379 (1926).

The device of superposing direct and radio-frequency currents in the specimen simultaneously, offered some promise as a means for making sure that both sets of measurements corresponded to exactly the same temperature. Figure 4 shows a typical pair of transition curves obtained with the longer tin specimen when a direct current of 69 ma and a current of 136 ma (rms value) at a frequency of 200 kc/s were superposed. Curve I shows the effective a-c resistance (expressed as a fraction of the normal a-c resistance above the transition range) plotted against temperature. Curve II gives the a-c resistivity, taken as proportional to the square of the corresponding resistance; while curve III gives the d-c resistance (and resistivity) as a fraction of their normal d-c values. At 3.68° K it is seen that the specimen offers an appreciable resistance to the alternating current while at the same time it offers practically none to the direct current. This paradox is easily seen to result from the fact that the material in the "skin" is subject to a pulsating magnetic field having a crest value of 5 oersteds produced by the combined action of the d-c and a-c components of the current and that the a-c component of current is forced by self-inductive effects to flow in this resisting skin. The d-c component, however, can escape into the core which, with a maximum field of 1.3 oersteds due to the d-c component only, will still be of very low resistance. The amount of the effective displacement of curves II and III depends in such a complicated way upon the magnitude and phase relations of the alternating current at various depths in the "skin" that the data obtained by the superposition of the two types of current are not of much value in comparing transition temperatures.

In the case of the tantalum specimen, with its higher resistance, smaller radio-frequency currents could be used without loss of precision. The experimental procedure found best was to hold the specimen successively at two intermediate temperatures in the transition range, allowing a sufficiently long time (usually 4 minutes) for the specimen to come to temperature equilibrium with the bath. The temperatures were so chosen that both points fell within the central portion of the transition range where the resistance is varying almost linearly. The temperature corresponding to the attainment of half the normal resistance was computed by a linear interpolation between these two points. Data obtained by approaching both points from below agreed with those obtained from above, the average deviation being about 2 percent in resistance or 0.001° K. The results of the two most reliable sets of data are given in table 1. The mean difference between the d-c value and those at 3,500 kc/s is 0.010° K. These results were obtained with direct currents of 5 ma and with alternating currents which were 6 ma (rms) when the specimen was cold but which fell off to 4 ma when the resistance was fully restored. The effects of current should therefore have been nearly equal in the two cases except as the cyclic variation by carrying the alternating current to crest values higher than the d-c or root-meansquare values may have produced an effect. The total observed change in resistance through the transition at 3,500 kc/s was 35.7 ohms which is 43 percent more than the d-c resistance change. This may have been due in part to dielectric losses in the insulation of the leads. to a local circulation of current between the specimen and the capacitance of the leads, thus increasing the current in the former, and to

other extraneous effects. Also, if an appreciable part of the excess resistance was the result of a skin effect greater than the small amount calculated on the basis of an isolated straight wire, the temperature for the restoration of one-half the resistivity would be higher, and hence nearer to the d-c value, than the temperature for the restoration of one-half the resistance. In view of these possibilities the observed difference in transition temperature, while greater than the accidental errors of measurement, is perhaps not larger than can be accounted for by some factor such as those mentioned above.

TABLE 1.—Temperature at which tantalum specimen had one-half normal resistance

Date	Transition fo	Frequency	
Date	Direct current	Alternating current	Frequency
8/14/34 9/13/34	° K 3. 948 3. 947	° K {3. 945 {3. 939 3. 935	kc/sec 1,000 3,500 3,500

We conclude that there is no effect of frequency per se in the superconducting transition temperature up to the frequencies here used,  $3 \times 10^{6}$  c/s. This is in accord with the conclusion of Burton.<sup>7</sup> It is, of course, possible that there may be an effect at higher frequencies.<sup>8</sup>

# IV. MICRORESIDUAL RESISTANCE

The electrical methods described above for measuring effective resistance at radio frequencies gave directly only the total resistance of a complete circuit. The metal-clad construction of the liquefier prevented us from inducing currents in a complete superconducting circuit, as had been done by the workers at Toronto. The resistance, 0.7 ohm, of the longest tin specimen was so small compared to the minimum workable value of about 6 ohms in the external circuit, that there was little hope of obtaining satisfactory measurements by any method of differences. In view of this situation, an attempt was made to apply calorimetric methods which could separate the heating and hence the resistance in the specimen proper from that in the rest of the circuit.

The very low specific heat of metals at low temperatures and the high sensitivity in temperature measurement obtainable with a helium vapor-pressure thermometer in this range were favorable factors. However, difficulty in securing sufficiently good thermal insulation of the specimen and the long time required for thermal equalization to be attained throughout the specimen reduced our precision so seriously that the method was finally abandoned. The following paragraphs, however, summarize the meager results obtained.

The specimen consisted of 0.6 g of tin which had been extruded into wire 0.022 cm in diameter and 2.25 m long. This was wound into a

 <sup>&</sup>lt;sup>7</sup> E. F. Burton. The Phenomenon of Superconductivity, p. 73, University of Toronto Press (1934).
 <sup>8</sup> See McLennan, Burton, Pitt, and Wilhelm. Proc. Roy. Soc. (London) [A] 136, 52 (1932).

coil about 3 cm in diameter made in two sections, so connected that their magnetic fields were in opposition, to minimize induction effects in the walls of the liquefier. Adjacent wires were separated by a silk thread and successive layers by cigarette paper, the whole structure being cemented with collodion. A resistance thermometer consisting of 400 cm of phosphor-bronze wire 0.013 cm in diameter wound bifilarly and having a resistance at room temperature of about 44 ohms was embedded between the two sections of tin wire. A few centimeters of lead (Pb) wire were used between the main specimen and the copper wires running out of the liquefier. As lead is superconducting up to 7.7° K, it was expected that there would be no heating in these connecting wires, even during the check runs made with the temperature slightly above the transition temperature of tin.

The flow of heat down the copper wires into the liquefier proper was so great, however, that, in spite of repeated efforts to get good thermal contact between these wires and the upper chamber of the liquefier, the junction of the lead and the copper wires was appreciably warmer than the walls of the liquefier. When the space surrounding the specimen was pumped down to a vacuum sufficient to give moderate thermal insulation, the specimen took on an appreciable fraction of this temperature difference and was about 0.22° K warmer than the bulb of the vapor-pressure thermometer. When current was flowing in the specimen the heating in the copper wires could cause a change in this temperature difference. This effect, together with possible dielectric loss in the insulation between the layers of the specimen and the currents which may have been induced in the phosphor-bronze winding, in spite of its bifilar arrangement, constituted possible sources of heat, even if the specimen itself had zero resistance.

Some 75 calorimetric runs were made on three different days and with two different specimens. When the thermal insulation was good enough, the rise in resistance of the bronze thermometer wire produced by a measured current of radio frequency flowing in the specimen for a measured short time (10 to 15 sec.) was taken as measuring the heat developed in the specimens under the conditions of temperature, frequency, etc., then existing. This tacitly assumes that the specific heat is constant. The known variations of specific heat in this range are not such as to seriously affect the conclusion. When the thermal insulation was not so high the current was allowed to flow until the bronze had come to a steady temperature and the calculations of rate of generation of heat were based on comparisons of these ultimate temperature rises (usually less than 1° K). Runs were made below (at about 2.5° K) and above (at about 3.9° K) the transi-tion temperature of tin. In all cases some heating was observed and it is impossible to estimate precisely how much may have been due to the sources listed above. Table 2 gives the ratio of the effective resistance below the critical temperature to that observed at the same frequency above the transition. These figures are the average of a number of observations and indicate that the greater part at least of the resistance of tin vanishes below the transition even at radio frequencies.

 TABLE 2.—Ratio of heating observed at temperature below the transition temperature to that observed above the transition, tin sample

Frequency	Ratio <sup>1</sup>
Direct current	0.004
120 kc/s 220 kc/s	.02 .03
514 kc/s	.04

<sup>1</sup> These figures for the high-frequency currents are larger than the ratio of about 0.01 reported to the American Physical Society at its meeting in April 1933 because of the inclusion of additional data.

It may be noted that the ratio of a-c to d-c heating above the transition temperature was about 10:1 at 514 kc/s, which is in reasonable agreement with the value 8.5:1 calculated from the skin effect in a straight wire of the same diameter at this frequency.

The much greater resistance of the tantalum specimen made possible the use at radio frequency of a method of differences which served to separate the resistance of the specimen proper from that of the rest of the circuit. The total resistance of the circuit containing specimen, leads and milliammeter was measured by the resistancevariation method,<sup>9</sup> by noting the value,  $I_1$ , of the current at resonance with the circuit in normal condition, and the value  $I_2$  when a resistance  $\Delta R$  had been added, and the circuit again tuned. The original resistance of the circuit is then given by

$$R = \Delta R I_2 / (I_1 - I_2)$$

Let the resistances of the two leads running to one end of the specimen be denoted by A and B, respectively, and those of the two leads to the other end by C and D, the resistance of the specimen being X. By connecting in succession each of the six possible pairs of terminals to the tuned radio-frequency circuit, the external part of which has the resistance Y, six values of total circuit resistance can be determined. If there is no mutual action between the various leads these six values will be

$$R_{1} = A + B + Y$$

$$R_{2} = A + C + Y + X$$

$$R_{3} = A + D + Y + X$$

$$R_{4} = B + C + Y + X$$

$$R_{5} = B + D + Y + X$$

$$R_{6} = C + D + Y$$

Eliminating the lead and external-circuit resistances from these equations gives

$$2X = R_2 + R_5 - R_1 - R_6$$
, or  
 $2X = R_3 + R_4 - R_1 - R_6$ 

as two partially independent determinations of X.

<sup>9</sup> NBS Circular C 74, p. 180 (1924).

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By this method 48 such determinations were made of the resistance of the tantalum specimen at temperatures from 2.9 to  $3.6^{\circ}$  K, well below its transition of  $3.9^{\circ}$  K. Three of the measurements were discarded as they differed from a tentative mean value in which they were included by more than 6 times the average deviation of a single observation from this mean. The results from the remaining 45 determinations are shown in table 3. The second column gives the number of determinations made at each frequency; the third column, the algebraic mean of these results; and the fourth column, a measure of the precision of the items in the third column, this measure being obtained by dividing the mean value without regard to sign of the several determinations. It happens that the mean of all the values of resistance in the superconducting state comes out to be only -0.02 ohm, but the measurements should be considered as indicating merely that the microresidual resistance is less than 0.2 ohm, or 0.8 percent of the resistance just above the transition.

[Resistance just above transition=25 ohms]

Frequency	Number of meas- urements	Mean re- sistance	Avg. deviation $\sqrt{n}$
kc/s 500 1,000 1,500 2,000 2,500 3,000 3,500	2 4 7 7 7 7 11	$\begin{array}{c} Ohms \\ -0.25 \\ +.27 \\37 \\29 \\11 \\ +.02 \\ +.59 \end{array}$	$\begin{array}{c} Ohms \\ \pm 0, 18 \\ \pm, 18 \\ \pm, 22 \\ \pm, 12 \\ \pm, 11 \\ \pm, 25 \\ \pm, 28 \end{array}$
Mean		02	±.2

# V. CONCLUSIONS

In view of the foregoing results, the answers to the three major questions seem to be as follows:

1. The transition from the normally resisting to the superconducting state and back again, under the influence of a pulsating magnetic field, can take place with sufficient rapidity <sup>10</sup> to follow pulsations having a frequency of 200,000 c/s.

2. The change in transition temperature with frequency is probably zero up to  $3 \times 10^6$  c/s, the small observed shifts being in opposite directions in the two materials tried.

3. The microresidual resistance for high-frequency currents of a superconductor when well below its transition temperature is probably zero. If any resistance exists, these experiments show that it is less than 4 percent of the resistance just above the transition in the case of tin, and less than 1 percent, in the case of tantalum. In terms of the resistance at room temperature these limits are  $4 \times 10^{-5}$  for tin and  $2 \times 10^{-3}$  for tantalum. These limits are unfortunately much larger than the corresponding limits for d-c measurements because of the experimental difficulties met in high-frequency work.

WASHINGTON, September 30, 1937.

<sup>10</sup> Other experiments (NBS J. Research 18, 295 (1937)) RP977, indicate that, at least in tantalum under certain rather limited conditions, a special type of transition may occur at a relatively very slow speed.