Fluxoid Quantization in a Multiply-Connected Superconductor*

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(Received 26 July 1963)

The transition temperatures of thin-walled superconducting hollow cylinders of very small diameters (approximately 1 μ) were measured as a function of the applied magnetic field in the axial direction. Oscillations with a period of $hc/2e$ in the magnetic flux through the cylinder were observed in the transition temperature T_c. This is a consequence of "fluxoid" quantization which was originally predicted by Fritz London. The basic unit of magnetic flux $hc/2e$ is explained in terms of London's original arguments and the result from the BCS theory that the charge carriers in a superconductor are pairs of electrons. Measurements were made on Sn, In, Pb, Al, and Sn-In alloys. A periodicity in the magnetic flux of $hc/2e$ was observed in all of the samples. The amplitude of ΔT_c varied from approximately 10^{-5} to 10^{-3}°K and depended upon the temperature, the radius, and the mean free path of the cylindrical sample.

I. INTRODUCTION

MORE than a decade ago, Fritz London[1] predicted that the "fluxoid," a quantity he defined as the sum of the magnetic flux and a term involving the persistent current, is quantized in units of hc/e in a multiply-connected superconductor. The fluxoid Φ is given by

$$\Phi = \int\int_S \mathbf{H} \cdot d\mathbf{S} + c \oint_P \Lambda \mathbf{J} \cdot d\mathbf{l}, \qquad (1)$$

where S is a surface bounded by the perimeter P, which contains a "hole" (where a "hole" refers to a real hole or a piece of nonsuperconducting material), J is the supercurrent, and the London parameter Λ has the value m/ne^2, where m is the mass of the electron, n the number of superelectrons, and e the charge of electron. In a superconductor the currents flow in a surface layer called the penetration depth whose thickness drops rapidly from ∞ at T_c, to a very small value of the order of 1000 Å at $T \ll T_c$. Thus, in a thick-walled, multiply-connected superconductor (e.g., a ring or hollow cylinder) at $T \ll T_c$, where the wall thickness is much greater than the penetration depth, the second term in Eq. (1) vanishes because we can now choose the integration path P to lie in a region of zero current flow. We are left with the result that the magnetic flux $\phi = \int\int \mathbf{H} \cdot d\mathbf{S}$ threading the hole in the superconductor should be quantized in units of hc/e (according to London).

The above situation was the experimental one realized by Deaver and Fairbank[2] and also by Doll and Näbauer[3] who reported simultaneously the observation that the trapped magnetic flux in a "thick-walled" superconducting cylinder at $T \ll T_c$ existed only in discrete quantum units. The startling result from both groups was the observation that the basic quantum unit was not hc/e as predicted, but rather $hc/2e$ (to an accuracy of 20–30%). This has been ascribed[4] to the fact that the charge carriers according to the BCS theory[5] are not single electrons, but rather pairs of electrons with a mass $2m$ and charge $2e$.[6]

We report here experiments in which we have examined a "thin-walled" superconducting cylinder at temperatures very close to T_c in an applied magnetic field in the axial direction. In this case, the penetration depth is very much greater than the wall thickness of the cylinder and we expect that the Meissner effect, which describes the expulsion of the magnetic flux, will be vanishingly small. This corresponds to a uniform magnetic field in the cylinder (both in the wall and in the interior) equal to the applied magnetic field. Thus, the first term in Eq. (1) is determined almost entirely by the applied magnetic field and the quantum periodicity must arise solely from the second term which describes the supercurrent.

II. PREDICTIONS

Consider a vanishingly thin superconducting cylinder with radius r in an axial magnetic field H. Using Eq. (1) and the value of the fluxoid $n(hc/2e)$, we obtain

$$J = ((nhc/2e) - \pi r^2 H)/2\pi rc\Lambda. \qquad (2)$$

The associated kinetic energy is

$$KE = \tfrac{1}{2}Nmv^2 = \tfrac{1}{2}\Lambda J^2 = \frac{\hbar^2}{16\pi^2 e^2 \Lambda r^2}\left(n - \frac{2e}{hc}\phi\right)^2, \qquad (3)$$

where $\tfrac{1}{2}N$ is the number, $2m$ is the mass, and v the average center-of-mass velocity of the pairs. This func-

[1] F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1950), Vol. 1.
[2] B. S. Deaver, Jr., and W. M. Fairbank, Phys. Rev. Letters 7, 43 (1961).
[3] R. Doll and M. Näbauer, Phys. Rev. Letters 7, 51 (1961).

[4] N. Byers and C. N. Yang, Phys. Rev. Letters 7, 46 (1961).
[5] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).
[6] Before any experimental results were reported, L. Onsager suggested that the value $(hc/2e)$ was a possibility because of the boson character of two-particle correlations in the superconducting state; W. M. Fairbank (private communication).
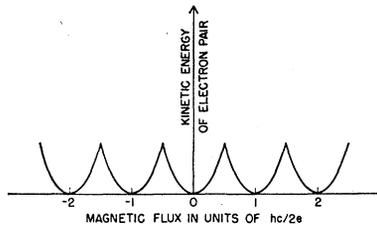
FIG. 1. Kinetic energy of the center-of-mass motion of an electron pair versus the magnetic flux.

tion is plotted in Fig. 1. We assume the integer n is allowed to change in value to keep the kinetic energy a minimum. As H is increased from zero with n zero, the kinetic energy increases quadratically. At $\phi = \frac{1}{2}(hc/2e)$, n switches from 0 to 1 and a further increase in H results in a decrease in the kinetic energy. At $\phi = \frac{3}{2}(hc/2e)$, n switches from 1 to 2, etc. Thus, the kinetic energy is periodic in the flux. As this kinetic energy contributes to the free energy of the superconducting phase, the free energy also must be periodic in the flux. On the other hand, one can easily show that free energy of the normal phase is essentially independent of the flux. Therefore, the transition temperature T_c which is determined by the temperature at which the free energy of the normal and superconducting phases are equal, must itself be a periodic function of the flux.

If we assume that the number of pairs and the pair interaction strength is independent of the flux, then the free-energy difference between the normal and superconducting phases consists solely of the kinetic energy difference discussed above. From this, one may readily calculate the change in the transition temperatures, ΔT_c. In our original prediction of 5×10^{-5}°K for ΔT_c for a 1-μ diam cylinder,[7] we took the number of pairs N to be the number of pairs of particles which are correlated in the BCS theory, i.e., the pair condensate. This is a small fraction of the total number of electrons and gave a result which disagreed with a calculation made by Tinkham[8] based upon the Ginzburg-Landau theory. Our error lay in confusing the BCS pairs with the superfluid component described by the London parameter Λ. A microscopic calculation using the equations of motion technique in the BCS theory[9] gives essential agreement with Tinkham's result, as it should, because the two theories agree with one another at the transition point. The result is

$$\Delta T_c = 0.14 \left(\frac{l}{\xi_0} \right) \left(\frac{E_f}{kT_c} \right) \frac{\hbar^2}{4mr^2 k} \left(n - \frac{2e}{hc} \phi \right)^2 , \qquad (4)$$

where l is the electronic mean free path, ξ_0 the Pippard coherence length, r the radius of the cylinder, m the electronic mass, and E_f the Fermi energy.

While the two methods give the same results, it is appropriate to point out that in Tinkham's derivation,

[7] W. A. Little and R. D. Parks, Phys. Rev. Letters **9**, 9 (1962).
[8] M. Tinkham, Phys. Rev. **129**, 2413 (1963).
[9] W. A. Little (to be published).

two statements are made which we believe are incorrect or at least misleading. He equates the number of pairs to half the number of superelectrons and applies what is equivalent to the Bohr-Sommerfeld quantum condition to these pairs. The number of particles which are correlated with one another as pairs and which can be treated as bosons with charge $2e$, is the number of particles in the pair condensate. Clearly, this condensate can involve only a small fraction of the total number of electrons, for in the theory, the electron-electron interaction which provides the binding of these pairs is attractive only in the vicinity of the Fermi surface. However, the number of superelectrons *is* of the order of the total number of electrons. Hence, it is obvious that the number of pairs is not half the number of superelectrons. Secondly, while it is correct to apply the Bohr-Sommerfeld condition to the pairs (with the charge $2e$) in the pair condensate, it is not correct to apply this same condition to the electrons (charge e) which lie deep within the Fermi sea where they are not correlated as pairs. Furthermore, the microscopic theory shows that it is not *the kinetic energy of the pairs* which raises the free energy of the superconducting phase as assumed by Tinkham, but rather it is due to *the difference in the energy* of the two members of the pair. The remarkable feature about this is that in spite of these differences, the two methods of approach, Tinkham's and the microscopic, give identical results.

The reason for this is that the "number of superelectrons" is really a product of terms, one of which is the number of electrons in the pair condensate, and another in the square of the difference of the energy of two members of the pair. Upon evaluating the difference, one obtains a factor of the order of (E_f/kT_c) times the kinetic energy of one pair. This first factor increases the effective number of pairs from that of the condensate to a number comparable to the total number of electrons. The second allows one to treat the problem
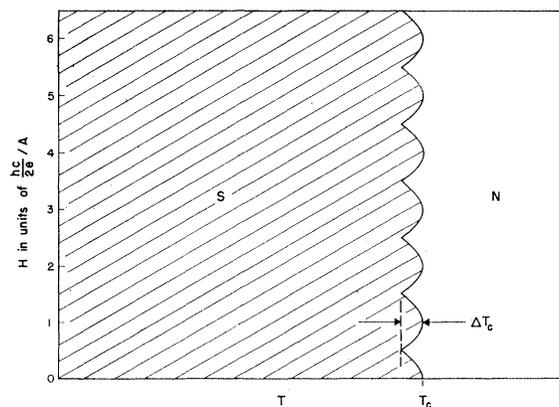

FIG. 2. Phase diagram of a thin cylindrical superconductor in an axial magnetic field. The scalloped edge of the superconducting phase is a consequence of the periodicity in the free energy of the superconducting phase with the magnetic flux through the cylinder.

as if the free-energy increase *is* due to the kinetic energy of the superelectrons.

We will see that it is difficult to obtain a meaningful value of ΔT_c (in terms of comparing it with theoretical predictions) from the experimental results. Therefore, we shall not consider further the evaluation of ΔT_c.

III. EXPERIMENTAL DETAILS

1. Sample Preparation

In order to obtain the necessarily small cylindrical formers upon which the superconducting metal was later to be evaporated, we prepared very thin organic fibers in the following way. A small droplet of GE-7031 insulating varnish was supported on the tips of two wires. Then the wires were quickly pulled apart. The resulting fiber varied in size from approximately 0.5 to 10 μ depending upon the size of the initial droplet and the rate of drawing. The fiber was mounted over a 2-mm diam hole on a specially prepared glass slide. A coating of the metallic superconductor over the entire surface of the fiber was obtained by rotating the glass slide (with the axis of rotation coinciding with the axis of the fiber) in a vacuum evaporator.

Evaporations were carried out in the pressure range 1×10^{-6}–1×10^{-5} mm Hg. Typical distances between the sample and the source were 20–30 cm. Film thicknesses were determined from measurements of the amount of metal evaporated from an "effective point source." The diameters of the fibers were determined by observing the diffraction pattern of the reflected light from the fiber. Electron microscopy was employed as a check on this method.

These methods provided an accuracy of 5% in the measurement of the diameter of the fibers. Microscopic examination of specimens of tin, indium, and lead prepared in the above way revealed that the metallic surface was not smooth but very rough owing to the formation of macroscopic crystals in the film. This is not uncommon in metallic films of low melting-point metals which have been deposited on warm or ambient temperature substrates. This problem is conventionally solved by cooling the substrate (usually to liquid nitrogen temperatures). However, because of the geometry of the fiber substrate, cooling could not be employed. Some improvement in the quality of the films was obtained in increasing the source to sample distance and, initially, by using a thin priming layer of gold. The aluminium films were of much higher quality than the tin, indium, and lead films.

2. Cryogenics and Electrical Measurements

The glass slide supporting the fiber was situated directly in a liquid helium bath. The temperature was stabilized above the λ point (2.19°K) with a diaphragm manostat and below the λ point with an electronic control system. Temperature stability of 10^{-5}°K was ob-
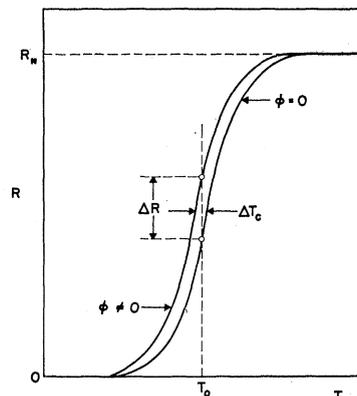

FIG. 3. Typical variation of resistance with temperature of a thin cylindrical superconductor showing how small changes ΔT_c in the transition temperature can be determined by measuring the change of resistance ΔR while holding the temperature constant at T_0.

tained. The temperature was measured with carbon resistors which were part of a 100 cps phase-sensitive, lock-in Wheatstone bridge. The resistors were calibrated in each run against the vapor pressure of liquid helium. A solenoid situated in the helium bath provided the necessary magnetic fields (0–100 G).

The measurements were made in the following manner. The resistance, which was used to determine T_c, was measured by passing a small dc current through the cylindrical film and measuring the potential drop across it. The currents used were of the order of 10 μA which corresponds to current densities of the order of 10^3 A/cm^2 in the samples used. The magnetic field at the sample was varied sinusoidally and the resulting variation in the resistance of the film was observed. From the observed oscillations in the resistance R, it was possible to calculate the oscillations in T_c. The relation between ΔR and ΔT_c is shown in Fig. 3. The resistive transition curve corresponding to $\phi=0$ (or $H=0$) displays the temperature broadening which is characteristic of thin film resistive transitions. If $H\neq0$, the transition curve is displaced to a lower temperature. Therefore, if at some temperature T_0, ϕ (or H) is increased, there is a corresponding increase in the resistance, ΔR. Then if the R versus T curve is known, the corresponding decrease in the transition temperature ΔT_c can be calculated.

IV. EXPERIMENTAL RESULTS

1. General Features

In the measurements, the axial magnetic field was varied sinusoidally and the induced voltage response across the fiber was displayed on an oscilloscope and photographed. The results for a tin sample are shown in Fig. 4. In (b) the display is amplified to illustrate the precision with which one can measure the periodicity. In both (a) and (b) the center point in the symmetrically scalloped spectrum corresponds to zero magnetic field. The period of the small parabolic scallops is $hc/2e$ in the magnetic flux as predicted. An unexpected result was the nonperiodic quadratic background which appeared in all of the samples and which varied in magnitude depending upon the diameter of the cylindrical sample,
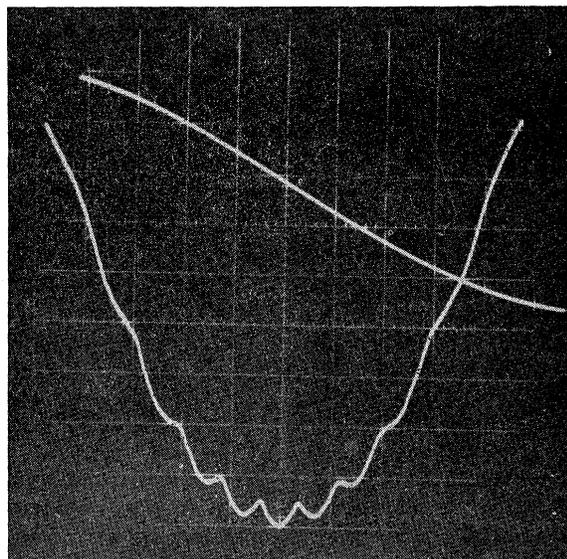
(a)
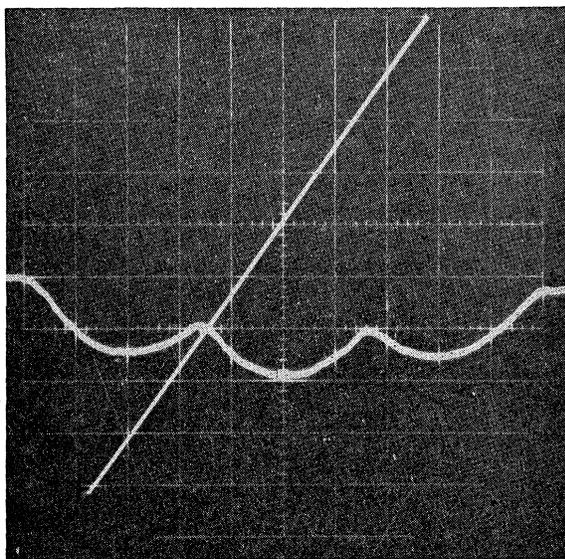
(b)

FIG. 4(a). Lower trace: Variation of resistance of tin cylinder with magnetic field at its transition temperature showing a periodic parabolic array superimposed upon a quadratic background. Upper trace: magnetic field sweep. (b). The same as (a) except lower trace is electrically magnified.

the wall thickness, and the orientation of the sample in the magnetic field. A thorough and quantitative investigation of the dependence of this effect upon these parameters has not been completed.

Results similar to those for the tin sample in Fig. 4 were obtained with samples of In, Pb, Al, and various Sn-In alloys. The results for an In sample and an Al sample are shown in Figs. 5 and 6. In all of the samples, the measured value of the basic flux quantum was $hc/2e$, with an error of less than 10% for In, Sn, and Al,

TABLE I. Summary of the properties of four Sn samples.

Sample	Composition	Diameter (μ)	Residual resistivity $(10^{-6}\ \Omega\ \text{cm})$	Film thick-ness (Å)
I	Sn	1.60	3.4	700
II	Sn	2.36	3.3	780
III	Sn–1% In	1.26	22.0	760
IV	Sn–1% In	2.40	22.0	800

and less than 20% for Pb. The accuracy in the case of the first three was limited by the measurement of the diameter of the fiber and in the case of Pb by poor temperature stabilization near the transition temperature of Pb which resulted in less clear oscillograms.

The ΔT_c oscillations were observed at frequencies from 5 to 2000 cps. Above 2000 cps direct pickup from the field source obscured the effect. In samples of large diameters (3–4 μ) as many as 60 quantum periods were observed in the oscillographs.

2. Dependence of ΔT_c Upon T, r, and l

According to Eq. (4), ΔT_c should be independent of T, should vary inversely as the square of the radius r, and should be proportional to the mean free path l. In order to test these predictions, we measured ΔT_c as a function of the reduced resistance R/R_N (R_N is the normal resistance) in a series of tin cylinders of various resistivities and radii. In Table I a summary of the properties of these samples is given. In order to obtain high resistivities corresponding to short mean free paths, a 1% In impurity was added to samples III and IV. This had very little effect upon T_c, but decreased
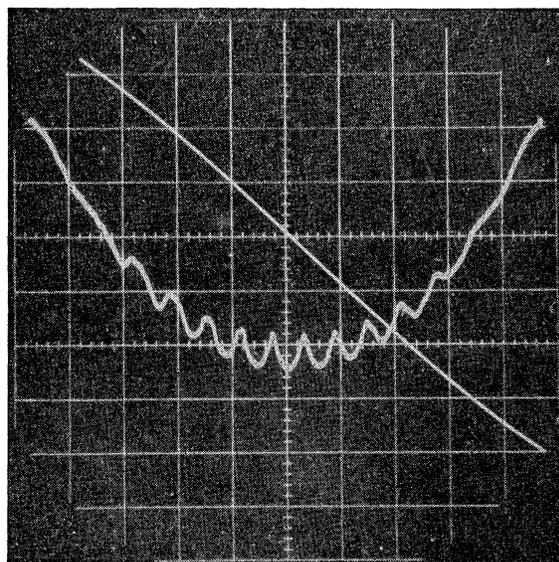

FIG. 5. Variation of resistance of an indium cylinder with magnetic field at its superconducting transition temperature.

the mean free path by approximately a factor of 7. The film thicknesses did not differ appreciably among the four samples.

In Fig. 7 the resistive transition and the dependence of ΔT_c upon T are given for sample I. This is typical of the results for the other three samples. Instead of being temperature independent as expected, ΔT_c increased very rapidly with decreasing temperature. These results are summarized in Fig. 8 where ΔT_c versus R/R_N curves are shown for the four samples. In order to determine the dependence of ΔT_c upon r, we combined all of the data from Fig. 8 to obtain the plot in Fig. 9. This plot relates ΔT_c to the reduced resistance R/R_N in terms of the negative exponent of the radius versus R/R_N. It was expected that such a plot would yield a horizontal line at the ordinant 2, corresponding to larger values of
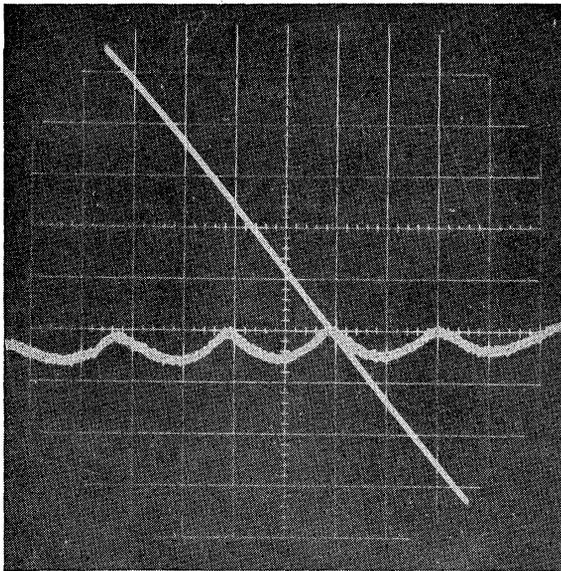

FIG. 7. Resistance and ΔT_c versus temperature curves for sample I in the transition region.

FIG. 6. Variation of resistance of an aluminum cylinder with magnetic field at its superconducting transition temperature.

R/R_N, ΔT_c deviates from the $1/r^2$ dependence and approaches perhaps an exponential dependence upon r. Because of the spread in the plot at higher temperatures, it is not possible to distinguish between an exponential and changing power law dependent on r.

In order to obtain the dependence of ΔT_c upon the

TABLE II. Values of $(\Delta T_c$ at $R/R_N)$ for samples I–IV.

Sample	I	II	III	IV
$(r/r_1)^2$	1.00	2.18	0.62	2.25
ΔT_c at $R/R_N=0$ $(10^{-4}\ °K)$	43	23	10.4	3.4
l/l_1	1.00	1.03	0.15	0.15
ΔT_c at $R/R_N=0$ Normalized to sample I with respect to $1/r^2$	1.00	1.16	0.15	0.18

mean free path, it is necessary to normalize the data in Fig. 8, taking into account the different radii of the samples. The most reliable method is to consider $(\Delta T_c$ at $R/R_N=0)$, where ΔT_c varies as $1/r^2$ (from Fig. 9). We then normalize l and r to sample I and obtain the results shown in Table II. When $(\Delta T_c$ at $R/R_N=0)$ is normalized to sample I with respect to $1/r^2$ (last line in Table II), it is seen that the agreement between ΔT_c and l/l_1 is quite good. The agreement is even better if only samples II and IV are considered since they are approximately of the same radii, which eliminates the required normalization. Thus, within experimental
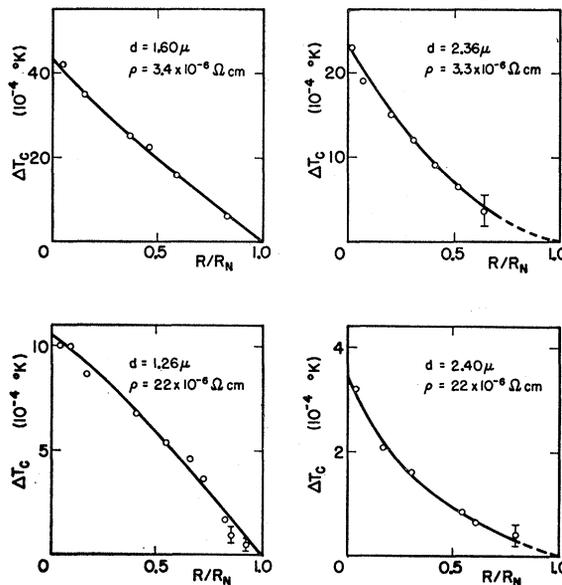

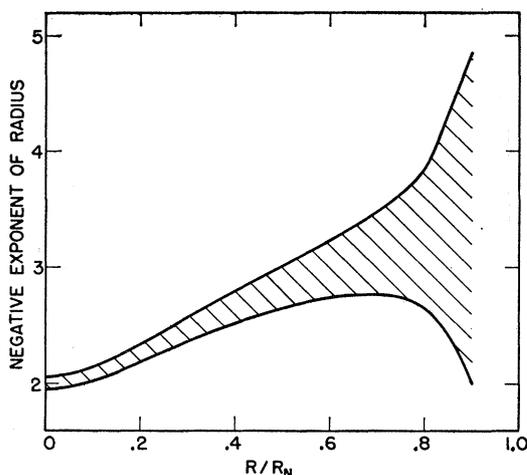FIG. 8. ΔT_c versus the reduced resistance R/R_N for samples I–IV.

FIG. 9. Display of the power-law dependence of ΔT_c upon the radius of the cylinder in terms of the negative exponent of the radius versus the reduced resistance R/R_N. All of the data from Fig. 8 is included in the shaded plot.

error, ΔT_c is proportional to the mean free path l as predicted.

V. DISCUSSION

1. Nonperiodic Quadratic Effect

There are several factors which probably contribute to the nonperiodic quadratic background in Figs. 4 and 5. One of the most obvious is the fact that if the ratio of the wall thickness to the diameter of the cylinder is finite, and if measurements are made at temperatures slightly below T_c, there will be a small Meissner effect and consequently a nonperiodic H^2 term in the free energy and, therefore, also in ΔT_c. A less obvious factor is one which appears in a microscopic theoretical analysis by Little.[9] It is found that the free-energy difference between the superconducting and normal states depends upon the difference in the single-particle excitation energies of the two members of an electron pair. If the members of the pair are electrons with oppositely oriented spins, the interaction of their magnetic moment with the magnetic field leads to an additional energy difference between the electrons which corresponds to a nonperiodic quadratic term in H. Both of the above explanations predict an effect which is much smaller than the observed one (by one or two orders of magnitude) and one which is not very sensitive to the alignment of the cylinder in the magnetic field, which was found to be important in the experiments.

A more speculative explanation offered by Tinkham[8] is the following. If there is a component of the magnetic field perpendicular to the axis of the cylinder, corresponding to a misalignment of the cylinder in the field, vortices of the "Abrikosov type"[10] will form on the sides

[10] The existence of vortices in simply-connected superconductors under certain conditions was first discussed by A. A. Abrikosov

of the cylinder (with their axes of rotation perpendicular to the axis of the cylinder). This contributes also to a nonperiodic, quadratic term in H. This effect is larger by two orders of magnitude than the other effects described and is very sensitive to the alignment of the cylinder in the magnetic field, thereby agreeing more closely with the qualitative experimental results. However, the experimental analysis of this effect is too incomplete to provide a basis for distinguishing between the contributions from these various factors.

2. Dependence of ΔT_c upon r

The results in Fig. 9 can be explained at least in a qualitative sense if we imagine that a heterogeneous mixed state of superconducting and normal metal prevails in the cylinder at the upper end of the resistive transition. This is illustrated in Fig. 10. A large number of macroscopic superconducting regions are shown immersed in a sea of normal metal.[11] This could be due to a spatially varying attractive electron-electron interaction due to impurity and strain effects in the cylindrical films. In order for the ΔT_c effect to be observable, a pair must traverse the circumference. We suggest that
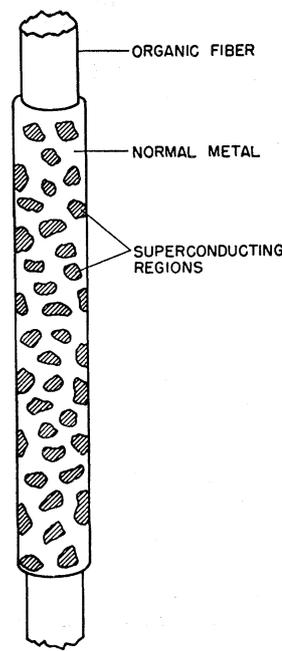

FIG. 10. Illustration describing the heterogeneous mixed state, consisting of superconducting and normal regions, which may occur in a thin hollow cylinder at the high-temperature end of the superconducting transition.

where he considered type II superconductors in bulk form: A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. 32, 1442 (1957) [translation: Soviet Phys.—JETP 5, 1174 (1957)]. Tinkham (Ref. 8) considers the case of a thin superconducting film in a perpendicular magnetic field.

[11] We should expect that the minimum size of the superconducting regions is determined by the coherence distance ξ. If we determine ξ from the relation $1/\xi = 1/\xi_0 + 1/l$, where l is the mean free path in the normal state and for ξ_0, we choose the value, 10^{-4} cm (see Ref. 5); we obtain values for ξ of approximately 100–1000 Å) for the samples studied. This is much shorter than the circumferences of the cylinders; therefore, the picture in Fig. 10 is feasible at least with respect to this consideration.

this is possible even in the situation depicted in Fig. 10. Since a BCS pair has a finite lifetime in the normal metal,[12] there will be a finite probability that the pair can traverse one of the normal "straits" between superconducting regions. The probability that the pair will traverse the entire circumference, and, therefore, the amplitude of ΔT_c, will be proportional to the quantity $\exp(-An)$, where n refers to the number of normal metal barriers on a particular circumferal circuit and A relates to the probability that the pair can get through one of the barriers (assumed for simplicity to be of equal size). Of course, n is just proportional to the radius of the cylinder r. We then have

$$\Delta T_c \propto (e^{-Br}/r^2), \qquad (5)$$

where B is a constant which depends upon the "mixed state" description and which vanishes at lower temperatures, where the mixed state of the cylinder can be described in terms of broad bands of superconducting material which completely girth the cylinder and which are separated by narrow bands of normal metal. Equation (5) is in qualitative agreement with the results in Fig. 9.

3. Dependence of ΔT_c Upon T

The increase in ΔT_c with decreasing temperatures (Fig. 7) can be explained also, in terms of the "mixed state" picture shown in Fig. 10. If, for purposes of illustration, we assume that the superconducting regions are very large and of uniform size, then the resistive transition in zero magnitude field would be that shown in Fig. 11, where we have assumed that the transition temperature of each superconducting region is different. This situation is, of course, implied by the breadth of the resistive transition shown in Fig. 7. We now assume that in the presence of the magnetic field there are two effects; the temperature at which each region becomes superconducting is lowered and secondly, the spatial extent of each superconducting region is decreased. This leads to the displaced transition curve corresponding to $H=0$ in Fig. 11. It is clear that the two transition curves diverge at lower temperatures. Therefore, if ΔT_c is measured at the upper end of the resistive transition, a smaller value will be obtained then if the measurement

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[12] Experiments and theoretical considerations which relate *indirectly* to the "lifetime of Cooper pairs" or the "persistence of superconductivity" in a normal metal have been reported by various authors. For example, see, D. H. Douglass, Jr., Phys. Rev. Letters **9**, 155 (1962); and L. N. Cooper, Phys. Rev. Letters **6**, 698 (1961).
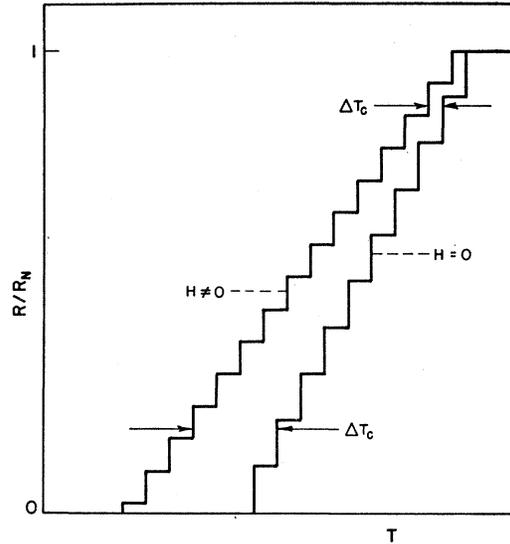

Fig. 11. Predicted resistance versus temperature curves for a superconductor which is in a mixed state such as that illustrated in Fig. 9. For simplicity it is assumed that the superconducting regions are of uniform size; and they are exaggerated in size. It is also assumed that the effect of the magnetic field is to suppress the temperature at which each region goes superconducting and to decrease the spatial extent of each superconducting region.

is made at the lower end. This agrees with the results in Fig. 7.

VI. CONCLUSIONS

In conclusion we note that this technique gives an extremely precise measure of the flux quantum, it gives further evidence of pairs in the superconducting state, and direct evidence of the periodicity of the free energy in a multiply-connected superconductor. We observed also that the amplitude of the changes in T_c is proportional to the mean free path as predicted. However, the presence of a mixed state of normal and superconducting regions in the samples has complicated the experimental situation and has made it difficult to obtain a meaningful value for the magnitude of the ΔT_c oscillations which can be compared with theoretical predictions. We believe that by using samples of smaller diameter and by improving the film deposition techniques, this difficulty can be overcome. Progress is underway towards this end.

(a)

(b)
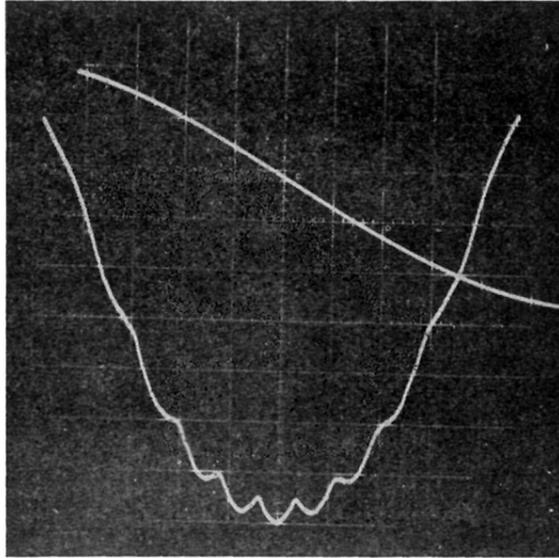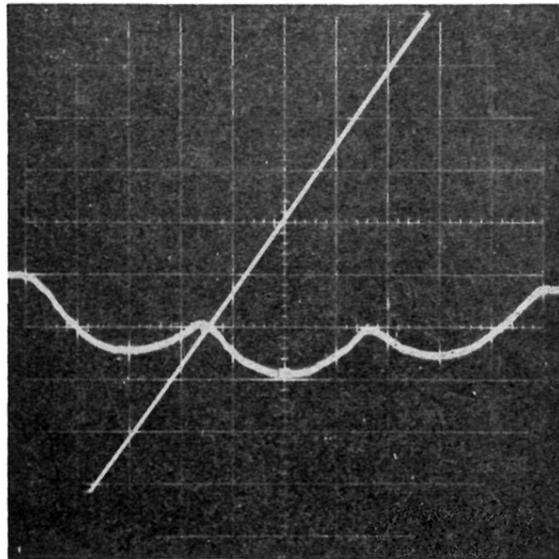
FIG. 4(a). Lower trace: Variation of resistance of tin cylinder with magnetic field at its transition temperature showing a periodic parabolic array superimposed upon a quadratic background. Upper trace: magnetic field sweep. (b). The same as (a) except lower trace is electrically magnified.
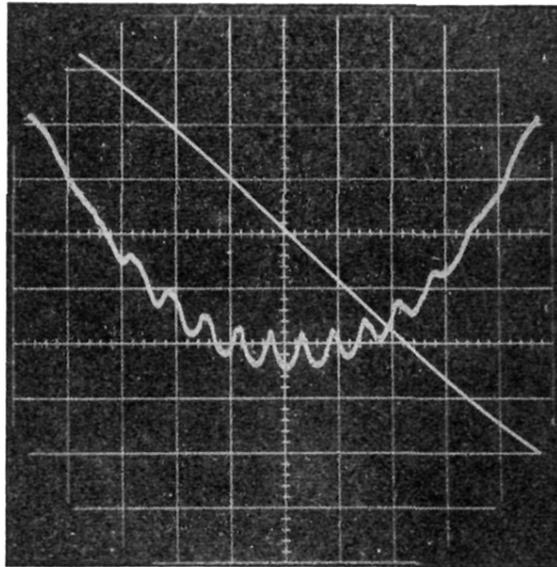
FIG. 5. Variation of resistance of an indium cylinder with magnetic field at its superconducting transition temperature.
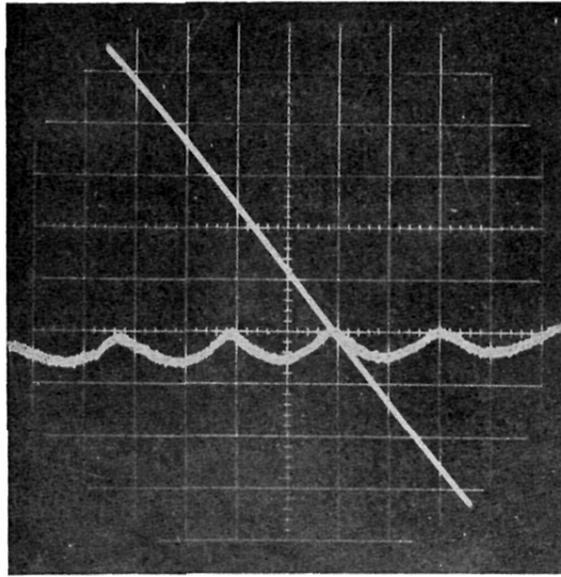
Fig. 6. Variation of resistance of an aluminum cylinder with magnetic field at its superconducting transition temperature.