multiplying $\sigma_\mu$. This identity leads to

$$c_{p\sigma}{}^\dagger c_{p'\sigma'}=\tfrac{1}{2}\sum_{\lambda=0}^{3}\langle\sigma'|\sigma_\lambda|\sigma\rangle(\mathbf{c}_p{}^\dagger\sigma_\lambda\mathbf{c}_{p'})\,, \qquad \text{(C9)}$$

by means of which the alternative proof of Eq. (5.7) is given. Equation (5.4) is a direct consequence of Eq. (C8). Introducing Eq. (C9) into Eq. (3.1), we get

$$\langle\mathbf{p}_1\sigma_1\mathbf{p}_2\sigma_2|G(t-t')|\mathbf{p}_3\sigma_3\mathbf{p}_4\sigma_4\rangle$$
$$=-i\tfrac{1}{4}\sum_{\lambda,\mu=0}^{3}\langle\sigma_2\sigma_3|\sigma_\lambda{}^{(1)}\sigma_\mu{}^{(2)}|\sigma_1\sigma_4\rangle$$
$$\times\langle T[\mathbf{c}_{p_1}{}^\dagger(t)\sigma_\lambda\mathbf{c}_{p_2}(t)\mathbf{c}_{p_4}{}^\dagger(t')\sigma_\mu\mathbf{c}_{p_3}(t')]\rangle. \qquad \text{(C10)}$$

Because of Eq. (C7), the terms with $\lambda\neq\mu$ vanish on the right-hand side if we refer to the paramagnetic ground state; this proves Eq. (5.8).

We shall now prove Eq. (5.20). For $n=1$, we have

$$\langle\mathbf{p}\sigma_1\mathbf{p}+\mathbf{q}\sigma_2|[G^{(0)}(\omega)V]|\mathbf{p}'\sigma_3\mathbf{p}'+\mathbf{q}\sigma_4\rangle$$
$$=\tfrac{1}{4}\sum_{\mathbf{p}''\sigma_5\sigma_6\lambda}\langle\sigma_2\sigma_5|\sigma_\lambda{}^{(1)}\sigma_\lambda{}^{(3)}|\sigma_1\sigma_6\rangle\langle\mathbf{p}|G_\mathbf{q}{}^{(0)}(\omega)|\mathbf{p}''\rangle$$
$$\times\{\langle\sigma_6\sigma_3|\sigma_5\sigma_4\rangle\langle\mathbf{p}''|V_\mathbf{q}{}^s|\mathbf{p}'\rangle$$
$$+\langle\sigma_6\sigma_3|\boldsymbol{\sigma}^{(3)}\cdot\boldsymbol{\sigma}^{(2)}|\sigma_5\sigma_4\rangle\langle\mathbf{p}''|V_\mathbf{q}{}^t|\mathbf{p}'\rangle\}$$
$$=\tfrac{1}{2}\delta_{\sigma_1\sigma_2}\delta_{\sigma_3\sigma_4}\langle\mathbf{p}|G_\mathbf{q}{}^{(0)}(\omega)V_\mathbf{q}{}^s|\mathbf{p}'\rangle$$
$$+\tfrac{1}{2}\langle\sigma_2\sigma_3|\boldsymbol{\sigma}^{(1)}\cdot\boldsymbol{\sigma}^{(2)}|\sigma_1\sigma_4\rangle\langle\mathbf{p}|G_\mathbf{q}{}^{(0)}(\omega)V_\mathbf{q}{}^t|\mathbf{p}'\rangle, \qquad \text{(C11)}$$

where use has been made of

$$\mathrm{Tr}\{\sigma_\lambda\sigma_\mu\}=2\delta_{\lambda\mu}. \qquad \text{(C12)}$$

This proof is sufficient to see that if Eq. (5.20) is valid for $n$, it is for $n+1$. Therefore by mathematical induction, Eq. (5.20) holds for any $n\geqslant 1$.

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PHYSICAL REVIEW VOLUME 135, NUMBER 4A 17 AUGUST 1964

# Fluxoid Conservation by Superconducting Thin Film Rings*

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(Received 9 March 1964)

A torque method for measuring the persistent current in superconducting rings has been used to investigate the conservation of the fluxoid originally predicted by London. The fluxoid through a superconducting ring is composed of two parts, one describing the mechanical angular momentum of the electrons and the other the magnetic flux trapped by the ring. The mechanical angular momentum depends on the penetration depth λ and therefore on the temperature. If the fluxoid is conserved, temperature variations should alter the balance between the mechanical and electromagnetic angular momenta. As a consequence, the amount of trapped flux, and hence the persistent current, should vary with temperature even though the ring remains at all times entirely within the pure superconducting state with zero resistance. Very thin films of tin have shown experimentally a decrease in persistent current with increasing temperature and an increase with decreasing temperature which agree with that to be expected on the basis of the fluxoid conservation predicted by London.

## I. INTRODUCTION

THE possibility of inducing persistent circulating currents in superconducting rings is one of the most intriguing and least understood consequences of the vanishing of electrical resistivity in superconductors. Such a persistent current loop possesses a magnetic moment and holds "trapped" a magnetic flux equal to the product of the self-inductance of the ring and the persistent current. While the current-carrying state is by no means the ground state of the system it is nevertheless extraordinarily stable. The earliest investigations of persistent currents were in fact directed toward use of this stability as a means of establishing an upper limit on the possible resistivity of the superconducting state.

Much recent interest has centered on investigation of the suggestion, first made by London, that the "fluxoid" or action integral, taken around the ring, of the canonical momentum of the superconducting electrons should be both conserved and quantized. The fluxoid contains one term in the mechanical angular momentum of the electrons and one in the magnetic flux trapped by the ring. In typical experiments performed with superconducting rings, the mechanical angular-momentum term makes only an extremely small perturbation on the much larger magnetic flux term. It may be noted in passing that the situation in atoms is just the converse with the magnetic flux acting as the small perturbation (Zeeman effect). Several investigators[1,2] using cylinders for which the mechanical angular-momentum term

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[1] R. Doll and M. Näbauer, Phys. Rev. Letters 7, 51 (1961).
[2] B. S. Deaver and W. M. Fairbank, Phys. Rev. Letters 7, 43 (1961).

would be expected to be negligible have observed that the magnetic flux trapped by these cylinders is quantized.

The microscopic theories as well as the London theory predict that the fluxoid is a conserved quantity and each of these theories demands that variations of the ring temperature alter the relative portions attributable to the trapped flux and to the mechanical angular momentum of the electrons.

A consequence of such a redistribution is that the trapped flux and hence the persistent current in a ring should vary with temperature even though the ring remains in the zero-resistance pure superconducting state at all times. To date none of the theories indicates the detailed mechanism by which the redistribution takes place, but each predicts, within its own approximations, specific changes in the flux as a function of temperature. The present investigation was undertaken to determine whether these consequences of the conservation of the fluxoid can be observed and, if so, to what extent the observations conform to the predictions of theory.

## II. ANALYSIS AND DISCUSSION OF THE FLUXOID PROBLEM

In 1948 when London[3] showed that his phenomenological theory predicted conservation of the fluxoid by a superconducting ring, he noted further that quantization of the fluxoid is implied by the usual quantum-mechanical assumption that the wave function of the superconducting charge carriers is single valued. More recently several authors[4–10] have treated the problem of the flux trapped by a hollow superconducting cylinder using a variety of approaches to obtain the electron-pair wave function. The results concerning the flux, however, depend principally on the assumption that the charge-carrier wave function is single valued. These various approaches yield a result which may also be obtained merely by application of the Bohr-Sommerfeld quantum condition to the charge carriers. The quantum condition simply states that

$$\oint \mathbf{p}\cdot d\mathbf{l}=kh\,, \tag{1}$$

where $\mathbf{p}=m^*\mathbf{v}+e^*\mathbf{A}$ is the canonical momentum of the pairs in a magnetic field, $k$ is an integer, $h$ is Plank's constant and $e^*$ and $m^*$ are the effective charge and mass of an electron pair.

If we denote by $n_e$ the effective number density of electron pairs, then the current density is given by $\mathbf{j}=n_e e^*\mathbf{v}$ and the penetration depth $\lambda$ is given by the usual relation

$$\lambda=(m/\mu_0 n_e e^{*2})^{1/2}. \tag{2}$$

In this work we shall consider only films whose thickness $\delta$ is very much less than $\lambda$ and the current density $j$ will thus be essentially uniform over the film thickness. There is substantial experimental evidence that for these thin films $j$ is uniform also over the cylinder length.[11] The trapped flux $\varphi$ is related to the persistent current $I$ by the expression $\varphi=LI$ where $L$ is the self-inductance of the cylinder. Using the well-known[12] inductance relation for a cylindrical-current sheet we may then write, using Eqs. (1) and (2) the flux expression

$$\varphi=\frac{kh/e^*}{1+2\lambda^2/\kappa r\delta}\,, \tag{3}$$

where $\kappa$ is Nagaoka's constant as it appears in the inductance relation and $r$ is the ring radius.

The simple analysis discussed here is essentially in the form suggested by London. The other analytical approaches alluded to above also yield Eq. (3) and differ only in the details of their predictions for the dependence of $\lambda$ on mean free path and temperature. Equation (3) is a consequence of the basic electrodynamic properties of the superconducting state and does not depend on the specific microscopic model used to arrive at these properties. It has been assumed here that all of the individual electron-pair wave functions have exactly the same number of nodes $k$, or that an average quantum number $k$ may be used. This latter assumption is implicit in treatments employing a self-consistent field approach to these problems. The treatment of this many-body problem by other than a self-consistent method appears grossly impractical but, even more to the point, such an individual particle treatment may not be meaningful since the physical quantities of interest, trapped flux and persistent currents, are macroscopic collective properties.

Bardeen[5] was the first to note the implications of the temperature dependence of the penetration depth appearing in the denominator of Eq. (3). The penetration depth $\lambda$ becomes very large near the transition temperature and the observed temperature dependence, especially in the range near $T_c$, is described quite satisfactorily by the phenomenological Gorter-Casimir-London theory which yields $\lambda^2=\lambda_0^2(1-t^4)^{-1}$, where $\lambda_0$ is the penetration depth at $T=0$ and $t\equiv T/T_c$ is the reduced temperature.

If we make the conventional assumption that all the pairs are in the same state, Eq. (3) may be expected to hold and the quantum number $k$ should be an adiabatic invariant. Equation (3) thus predicts that the "quantum" unit of flux is a function of temperature and in particular that it decreases with increasing temperature. It should be made clear that in all of the present experiments the quantum numbers $k$ associated with

[3] F. London, Phys. Rev. **74**, 562 (1948).
[4] J. M. Blatt, Phys. Rev. Letters **7**, 82 (1961).
[5] J. Bardeen, Phys. Rev. Letters **7**, 162 (1961).
[6] J. B. Keller and B. Zumino, Phys. Rev. Letters **7**, 164 (1961).
[7] F. Bloch and H. Rorschach, Phys. Rev. **128**, 1697 (1962).
[8] H. Lipkin, Phys. Rev. **126**, 116 (1962).
[9] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **42**, 299 (1962) [English transl.: Soviet Phys.—JETP **15**, 207 (1962)].
[10] N. Byers and C. N. Yang, Phys. Rev. Letters **7**, 46 (1961).
[11] J. E. Mercereau and L. T. Crane, Phys. Letters **7**, 25 (1963).

the trapped flux and current are very large, generally of order $10^5$ to $10^7$. Individual quanta are not resolved by the present experimental technique. It should also be noted that the quantum hypothesis is not essential to the derivation of the temperature dependence of trapped flux indicated by Eq. (3). Conservation of the canonical momentum is to be expected also for a nondissipative classical system.

## III. EXPERIMENTAL DETAILS

### 1. Method and Equipment

In a current versus temperature diagram for a ring, the phase boundary between the true superconducting state which is coherent all the way around the ring, and the intermediate state is delineated by the curve of critical *persistent* current[13,14] as a function of temperature. Since experiments on fluxoid conservation are meaningful only in the pure superconducting state, the determination of the critical persistent current as a function of temperature is a required initial step.

The magnitude of the persistent current in a superconducting ring may be readily determined by mounting the ring as the "moving coil" in a galvanometer system. In the present experiments the ring in which persistent current was to be measured was suspended in the liquid-helium bath by a quartz torsion fiber. The persistent current was then determined in terms of the angle of deflection of the ring in a small measuring magnetic field $B_m$. The effects of the measuring field upon the persistent current are usually negligible for these experiments but may, in any case, be easily accounted for.

In a typical experimental run, a small magnetic flux (such that the associated persistent current is much less than critical) is trapped as the ring is cooled well below $T_c$. This persistent current is then carefully measured as a function of temperature thereby generating a "fluxoid curve" as the ring is slowly warmed to temperatures near $T_c$. In this experimental method it is the torque due to the current which is actually measured and the relevant critical phenomena also involve primarily the current. As a consequence, a shift in emphasis from the trapped magnetic flux to the persistent current consistent with the flux will be noted. The two are essentially equivalent however (since $\varphi = LI$). In these experiments the temperature was measured with a carbon resistance thermometer which was calibrated against the helium vapor pressure scale during the pump-down before each rum. The resistance comparison method used yielded a precision better than 2 mdeg and an absolute accuracy of approximately 15 mdeg.

[12] *Radiotron Designers Handbook*, edited by L. Smith (RCA, Harrison, New Jersey, 1953), p. 429.

[13] J. E. Mercereau and T. K. Hunt, Phys. Rev. Letters 8, 243 (1962).

[14] J. E. Mercereau and T. K. Hunt, in *Proceedings of the Eighth International Conference on Low Temperature Physics* (Butterworths Scientific Publications Ltd., London, 1963).

### 2. Noise and Sensitivity

From Eq. (3) and the expression for $\lambda^2(t)$ it may be seen that the principle percentage variation in the persistent current may be expected to occur very near $T_c$ in a range for which the critical persistent current is itself quite small. When measuring very small persistent currents such as those associated with films as thin as 100 to 300 Å, it is necessary to use fibers of such sensitivity that mechanical "noise" induced by boiling or convection in the liquid helium becomes a serious problem. This problem, however, can be resolved in a relatively simple fashion. A liquid-helium bath with a positive temperature gradient upward is stable and convection currents do not arise. It is in practice quite simple to establish this condition by first pumping down to some low temperature and then admitting warm helium gas above the bath until atmospheric pressure is reached. The surface of the helium is then at 4.2°K while, due to the low thermal conductivity of liquid helium above the $\lambda$ point, the temperature at the level of the ring and fiber is only rising slowly toward 4.2°K. Since the pressure in the system is much higher than the vapor pressure of the helium in the vicinity of the ring, no boiling occurs and the bath remains quiescent. Attempts to work below the $\lambda$ point have shown that helium II is an appreciably "noisier" environment than a bath stabilized in the above manner.

Experimentally the local temperature gradient in the ring vicinity is of order 0.01K°/cm and does not change appreciably with time during a run. Since the rings used in these experiments are 1 cm in diameter, the presence of this small temperature gradient does not remove the significance of the "ring temperature." The physical problem of the current behavior in the presence of this temperature gradient has been handled by the tacit assumption that over-all control is exerted by the warmest point, at the top of the ring. It is at this level that the carbon resistance thermometer is placed. Although in the presence of this gradient the number density of superconducting electrons will be a function of position around the ring, no conversion of electrons between the superconducting and normal states occurs. This is in distinct contrast to the process which takes place when the temperature of the entire ring is raised or lowered. The case of electric-current flow around a superconducting ring in a temperature gradient is quite analogous to the case of nondissipative fluid flow in a toroidal pipe of varying cross section. More fluid is to be found in the regions with a large cross section but the flow remains continuous.

In the experimental investigation of fluxoid conservation by this method one is limited in the useful number of points which can be taken on a given fluxoid curve. It is necessary to read the extremes of the omnipresent residual fluctuations in the position of the "galvanometer" light spot in order to obtain averages for determining the equilibrium position. Ususally the extremes of at least 6 to 10 swings are recorded and averaged for each point shown on curves such as those in Figs. 1–5. Since the half-period of a typical fiber-ring-substrate system is usually about 25 to 40 sec, the measurement of a single point may take several minutes. In order for the current-temperature relation to make sense the recorded points must be separated in temperature by more than the change in temperature with time which occurs during an actual reading process. The nature of the temperature gradient quieting method limits the useful range to temperatures greater than about 2.7°K and hence for tin to reduced temperatures $t \gtrsim 0.7$. It is, however, in this upper temperature range that the effect is largest so that this limitation is not a very serious one.

### 3. Sample Preparation

At any given temperature the fraction by which the low-temperature persistent current value has been reduced depends on the magnitude of the quantity $2\lambda_0^2/\kappa r\delta$. The observability of the effects due to fluxoid conservation may be greatly enhanced by appropriately choosing the properties of the superconducting ring so as to maximize this quantity.

Due to the combined features of the current-measurement method, manipulation of the ring radius and length is not very useful in increasing the observability of the persistent current variations predicted by Eq. (3). The major gain is achieved by using very thin films produced in a manner tending to promote extraordinarily large penetration depths. It is well known that the penetration depth increases markedly in the presence of scattering which reduces the electron mean free path below the coherence length $\xi_0$.[15] The tin films used in these experiments were made very thin to enhance surface scattering and were doped with indium to provide impurity scattering centers. A strip of the superconductor material was evaporated uniformly onto a rotating quartz tube which was maintained at liquid-nitrogen temperatures. The resulting ring-substrate combination was raised to room temperature for mounting before suspension in the helium bath. The tin films used were of order 100 Å thick and contained indium as an impurity in concentrations up to 2%. The relative concentrations were determined by evaporating carefully weighed charges to completion. The source materials were 99.999% pure tin[16] and similarly pure indium.[17] The survival rate of these thin films appears to be considerably enhanced if, while the substrate is still cold and very shortly after the evaporation, argon gas is admitted to the vacuum chamber and the system is permitted to warm up slowly thereafter. One of the films (Fig. 2) was evaporated from reagent grade tin[18] containing 0.002% lead as an impurity. In that case the evaporation was not carried to completion and a severe enhancement of the Pb concentration in the deposited film appears to have occurred due to the differential evaporation rates of lead and tin.

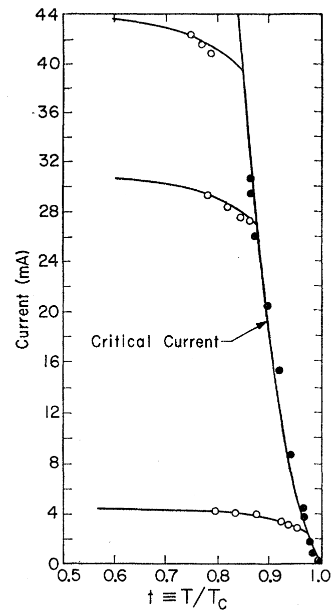


FIG. 1. Data showing the expected decrease of persistent current with increasing temperature in the pure superconducting state for a thin-film (110 Å) tin ring containing 1.9% indium. The solid curves are theoretical best fits to the data. The critical persistent-current curve shown is the phase boundary between the pure superconducting state and the intermediate state.

### 4. Flux Trapping Procedures

At temperatures $T_1$ below $T_c$ flux trapping is readily accomplished by applying and then removing a magnetic field normal to the plane of the ring which is larger than that needed to induce the critical current $I_c(T_1)$. The critical value is of course just $B=LI_c(T_1)/A$ where $A$ is the area of the ring hole. If a normal field larger than $B=2LI_c(T_1)/A$ is used there will be dissipation in the ring as the field is removed. This dissipation of energy can raise the ring temperature well above that of the bath $T_1$ and thus result in the "trapping" of a persistent current significantly less than the critical value $I_c(T_1)$.

## IV. EXPERIMENTAL RESULTS

### 1. Fluxoid Relation

"Fluxoid curves," showing persistent current as a function of temperature in the pure superconducting state, were investigated experimentally for several tin rings representing different compromises in the choice of film parameters. Very pure tin films were examined at thicknesses down to 350 Å, and alloy films containing up to 1.9% indium were examined at thicknesses down to 110 Å.

Figure 1 shows data from a series of fluxoid runs made on the 110 Å tin plus 1.9% indium ring. The data clearly show the expected decrease of persistent current with increasing temperature in the pure superconducting

[15] See, for example, D. H. Douglass, Phys. Rev. 124, 735 (1961).
[16] Supplied by A. D. Mackay, Inc., 198 Broadway, New York, New York, 10038.
[17] Supplied by Indium Corp. of America, Utica, New York.
[18] Baker Chemical Company, Phillipsburg, New Jersey.

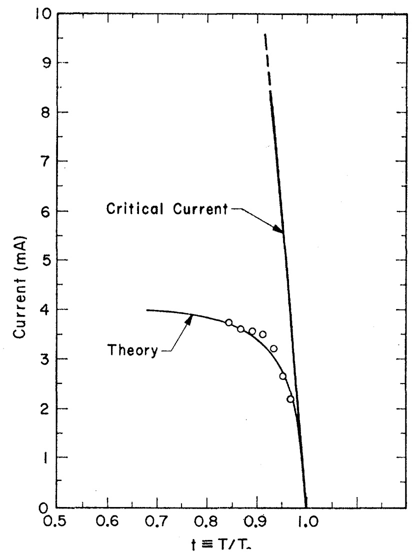


FIG. 2. A typical curve showing the decrease of persistent current with increasing temperature in the pure superconducting state for a 310 Å ring evaporated from reagent grade tin containing traces of lead as an impurity.

state. As predicted by the analysis, the greatest percentage decrease in the persistent current occurs near $T_c$ and this region is only accessible for low persistent-current values. While the percentage change is less at lower temperatures, much higher persistent-current values may be used while still satisfying the criterion of remaining entirely within the pure superconducting state at all times. The actual observable decrease in current is in fact somewhat larger for the latter case. Figure 2 shows representative data taken at quite low current values for the 310 Å lead-contaminated film which was evaporated from reagent grade tin.

In Figs. 1 and 2 the solid curves are plots of Eq. (3) with the quantity $2\lambda_0^2/\kappa r\delta \equiv C$ chosen in each case to yield the best fit for all fluxoid runs on the given ring. Equation (3) may be rearranged in the form $I(t)^{-1} = (C/I_0)y + I_0^{-1}$ which is more convenient for data analysis. In Fig. 3, $I(t)^{-1}$ is plotted as a function of $y \equiv (1-t^4)^{-1}$ for a typical run. The slope and intercept of the best straight line through the data yield the best-fit value of $C$ for the run. The good fit to a straight line on such a plot strongly attests to the adequacy of the description of the phenomenon advanced here. The value of $C$ used for the series of curves in Fig. 1 is an average of values obtained in this way for about 7 fluxoid runs on that ring.

Sample parameters and experimental values of $C$ for several rings are summarized in Table I. At this time there is no other published source of experimental results on penetration depths even in pure films as thin as the 110 and 150 Å films used here. Penetration-depth data on alloy films are not available even for considerably thicker films. The data of Mercereau and Crane[11]

TABLE I. Values of $(2\lambda_0^2/\kappa r\delta)$ for thin film rings as determined experimentally from the temperature dependence of persistent current in the pure superconducting state.

| Composition | Film thickness | $2\lambda_0^2/\kappa r\delta$ | $\lambda_0$ |
|---|---|---|---|
| Tin | 350 Å | 0−0.015 | <4500 Å |
| Tin + 1.0% indium | 150 Å | 0.082 | 7500 Å |
| Tin + 1.9% indium | 110 Å | 0.12 | 7700 Å |
| Tin + up to 0.3% lead | 310 Å | 0.12−0.15 | ~8400 Å |

on thin films of pure tin show a thickness dependence of the penetration depth in relatively good agreement with the theoretical work on mean free paths by Douglass.[15] If the theoretical curves of Douglass are extrapolated beyond the values he considers, to the shorter mean free paths associated with these very thin *and* impure films, the results yield values of $\lambda_0 \approx 6500$ Å. In view of the uncertainty of this extrapolation process and the notorious difficulty of producing good thin films of specified properties, this value agrees remarkably well with the penetration depths shown in Table I for the 110 and 150 Å films. The results of Mercereau and Crane on a pure tin film with $\delta = 350$ Å yield a penetration depth of about 1500 Å, well within the limits indicated here for the present 350 Å ring.

The experimental results show the expected temperature dependence of persistent current and the detailed variation with temperature corresponds to the usual temperature dependence of the penetration depth. This agreement and the quite reasonable values obtained for $\lambda_0$ attest to the applicability of the fluxoid conservation principle even under these rather extreme perturbations.

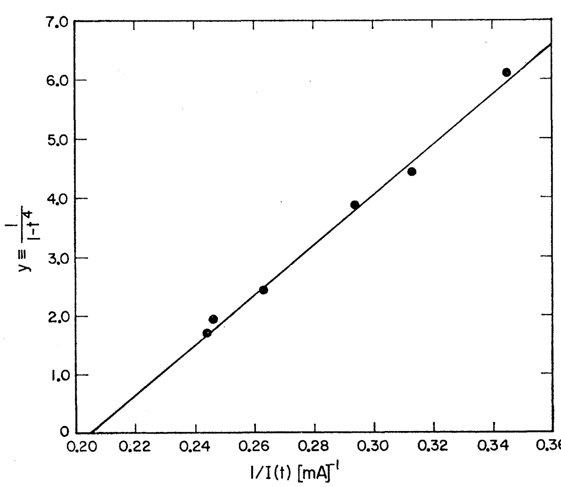


FIG. 3. Persistent current as a function of temperature plotted using the known temperature dependence of $\lambda$ to permit convenient evaluation of $C \equiv 2\lambda_0^2/\kappa r\delta$ and thereby of $\lambda_0$. The excellent fit of the data to a straight line in such plots confirms in detail the results of the analysis. Values of $C$ obtained in this way for all runs on a given ring were averaged to obtain the single value given in Table I. For this run on a tin-alloy ring $T_c = 4.065$°K, $\delta = 110$ Å, and $C = 0.112$.

## 2. Reversibility

If the number $k$ in Eq. (3) is a good quantum number under perturbations in the number of superconducting electrons (the basic effect of changing the temperature), then the persistent current carried by a superconducting thin film ring will actually *increase* as the ring is *cooled*, even in the absence of any applied magnetic fields. Investigation of such an increase of persistent current provides a further test of London's suggestion that superconductivity is a single quantum state of large extent. We shall discuss two approaches to the observation of this phenomenon.[19]

In the first approach the bath is slowly cooled down from 4.2°K and at an accurately known temperature $t_0$ one attempts to trap the entire critical persistent current $I_c(t_0)$. This current is subsequently measured at a lower temperature. Due to the orientation and dissipation problems one may actually trap significantly less than the critical value but if the current decrease phenomenon is irreversible, $I_c(t_0)$ would constitute the upper limit on the current which could ever be observed even at very low temperatures. On the other hand, if the phenomenon is reversible the upper limit at any given lower temperature is set by the fluxoid curve passing through $I_c(t_0)$ at $t=t_0$. Observation of low-temperature persistent-current values lying significantly above the "irreversible upper limit" is thus to be considered an indication that the phenomenon is not necessarily irreversible. While a number of runs yielded values well below both limits due to incomplete trapping, Fig. 4 shows an instance for the 110 Å ring in which the low-temperature persistent current lies distinctly above the "irreversible upper limit" as indicated, although it is still somewhat below the "reversible upper limit." An ordinary fluxoid curve was observed during the warm-up for this run as shown. The measurement of $t_0$ was made just after the initial trapping in order to be clearly on the safe side with respect to the temperature since the critical-current curve is quite steep in this range.

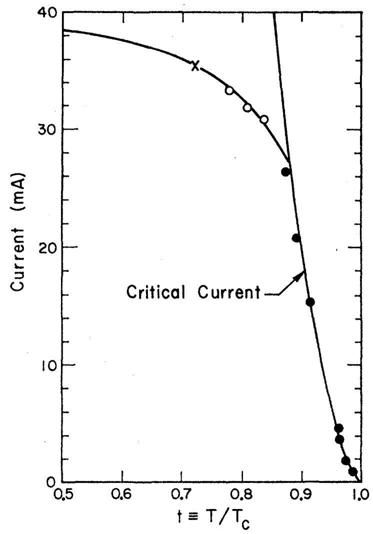


FIG. 5. Evidence for reversibility. The point shown with the cross was observed after pump-down following the recording of the circled points on the original fluxoid curve.

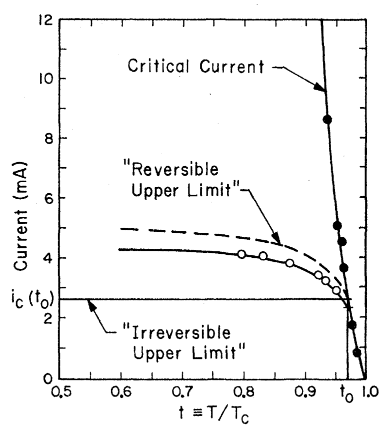


FIG. 4. Experimental results demonstrating the increase in persistent current with decreasing temperature expected on the basis of fluxoid conservation. At the temperature $t_0$ during the early stages of pump-down an attempt to trap the critical persistent current $I_c(t_0)$ was made. After reaching the minimum temperature the circled points were observed during the warm-up in the usual manner. The occurrence of low-temperature values significantly larger than $I_c(t_0)$ gives evidence that the current decrease phenomenon as shown in Figs. 1 and 2 is reversible.

Because it is always necessary to maintain a positive temperature gradient during the actual measurement of persistent current, it is not possible to take a series of datum points as the temperature is lowered by pumping on the bath. After a normal fluxoid run one can, however, pump back down to some low temperature, reestablish the positive gradient and then observe whether the low-temperature current significantly exceeds the lower current values observed on the original fluxoid curve.

The presence of the temperature gradient may, however, lead to difficulties in this approach to the study of reversibility. The turbulence associated with the early stages of the pump-down may mix the warmer liquid near the top of the bath with the cooler liquid in the vicinity of the ring. Thus a considerable overshoot in the temperature of the ring may occur. This thermal overshoot may under many circumstances be sufficient to drive the ring into the critical state and on down the critical-current curve thereby changing the quantum number $k$ as energy is dissipated in the ring. If this occurs it is quite possible that the subsequently observed low-temperature current value may actually be smaller than any of the values on the original fluxoid curve. This result was observed on several occasions. Figure 5 shows a run made with a relatively low initial helium level and for which the pump-down was initiated at a temper-

[19] J. D. Reppy and D. Depattie, Phys. Rev. Letters **12**, 187 (1964). These investigations of persistent currents in superfluid helium using an analog of the first approach discussed here, have shown an increase in the angular momentum of such persistent currents with decreasing temperature which corresponds to the temperature dependence of the superfluid density.

ature more than 0.2K° distant from the critical-current curve. In this experimental run the point denoted by a cross was measured after pump-down, following the recording of the three circled points on the initial fluxoid curve. The solid curve shown was fitted to these three points using the method discussed above. Within the limits of experimental error the point shown with a cross, measured after pump-down, falls on the same curve. The current variation in this experiment is thus *reversible* within the limits of experimental error.

A quite different approach has been used by Mercereau and Crane[20] to observe variations in the persistent current in rings whose temperature oscillates rapidly. In their experiment the ring comprises one wall of a cylindrical second-sound resonant cavity and a loosely coupled sensing coil is used to detect variations in the persistent current corresponding to the small ($10^{-3}$K°) temperature oscillations produced by the second sound. Under these more rapid perturbations the maximum possible reversible variation in the trapped flux appears to be only one "quantum" of flux.

[20] J. E. Mercereau and L. T. Crane, Phys. Rev. Letters **12**, 191 (1964).

## V. CONCLUSIONS

Persistent currents have been observed in thin films for which the film thickness is two orders of magnitude less than the penetration depth. In these films the field penetration is essentially complete and it is thus clear that the presence of a good Meissner effect is by no means essential for the stability of persistent currents.

The prediction that the fluxoid through a superconducting ring is conserved has been verified by an investigation of the temperature dependence of the magnetic flux trapped by such rings in the pure superconducting state. The experimental results show clearly both the decrease in trapped flux with rising temperature and an increase in trapped flux with falling temperature which are direct consequences of fluxoid conservation. Previous experiments carried out to observe flux quantization have explored only the properties of the electromagnetic part of the fluxoid since the effects of the mechanical term in those cases were negligible. The present experiments are sensitive to both terms comprising fluxoid and thus fill a conspicuous gap in the experimental picture of trapped flux and persistent currents in superconducting rings.

PHYSICAL REVIEW VOLUME 135, NUMBER 4A 17 AUGUST 1964

# Magnetic- and Electric-Field Effects of the $B_1$ and $B_2$ Absorption Lines in Ruby*

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(Received 17 March 1964)

A pseudo-Stark splitting of the $B_1$(20 993 cm$^{-1}$) and the $B_2$ (21 068 cm$^{-1}$) absorption lines in ruby has been observed at 2°K. The splitting of each $B$ line is $2.8\times10^{-5}$ cm$^{-1}$/V/cm for an electric field parallel to the $c$ axis. This is a factor 3.7 larger than the corresponding splitting of the $R$ lines. There is no observable effect for fields perpendicular to the $c$ axis. Crystal-field theory satisfactorily predicts these properties, which are determined by the symmetry of the $Cr^{3+}$ site. The point-charge model does not correctly predict the absolute value of the observed electric splitting, nor the matrix elements of the $B$ lines.

## I. INTRODUCTION

THE $B_1$ and $B_2$ absorption lines of the $Cr^{3+}$ ion in a lattice of $Al_2O_3$ were observed and named by Gibson[1] in 1916. Since that time, studies of these lines have been far less numerous and extensive than the studies of the narrower $R_1$ and $R_2$ lines which appear strongly in fluorescence as well as in absorption. In 1958 Sugano and Tanabe[2] identified the green and blue absorption bands and $R$ and $B$ lines with transitions to levels predicted by the crystal-field theory, reproduced in Fig. 1. Their predictions of the relative transition probabilities between the Zeeman components of each $R$ and $B$ line were partially confirmed by Sugano and Tsujikawa.[3] Since the latter's work was only semiquantitative, Schawlow, Varsanyi, and Wood[4] made a careful investigation of the $R_1$-line Zeeman structure and completely confirmed the predictions.[2] Wieder[5] detected microwave absorption between the $m=\pm\frac{3}{2}$ and $m=\pm\frac{1}{2}$ ground-state levels by observing the change in $R$-line optical absorption upon application of microwave power, and Geschwind, Collins, and Schawlow[6] used selective reabsorption of the $R_1$-line fluores-

* This research was supported jointly by the U. S. Office of Naval Research, the Signal Corps of the U. S. Army and the U. S. Air Force. Further details about the theory and experiment reported here may be found in the Ph.D. thesis of M. G. Cohen, Harvard University, 1963 (unpublished), or in Cruft Laboratory Technical Report No. 437.

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