Temperature dependence of the superconducting giant-vortex state. Theory and experiment

F. de la Cruz, H. J. Fink,* and J. Luzuriaga
Centro Atómico Bariloche,† *Instituto Balseiro,*‡
8400 S. C. de Bariloche, R.N., Argentina
(Received 3 January 1979)

When a type-I superconductor with a surface nucleation field $H_{c3}(T) > H_c(T)$ (thermodynamic critical field) is thermally cycled in an axially applied magnetic field H_0 between the temperatures $T(H_{c3})$ and about $T(H_c)$, experiments show that the magnetization changes reversibly. The latter is diamagnetic near $T(H_{c3})$ but can be paramagnetic just above $T(H_c)$. This behavior is explained by assuming that the fluxoid quantum number b is fixed at the transition from the normal to the superconducting state and retained at lower temperatures. The value of b is determined almost entirely by the flux at the transition which is enclosed by a contour located at a distance $\xi/1.7$ from the surface inside the cylinder (ξ is the coherence length). The temperature variation of the order parameter f at the surface of the cylinder, the magnetization m, and the temperature at which $m = 0$ for $f \neq 0$ are calculated for $R >> \xi$. Conservation of the fluxoid quantum number, while T is varied causes the two opposing surface currents to become imbalanced. This is the source of the observed para- and diamagnetism.

I. INTRODUCTION

In a previous publication[1] we have shown that the magnetization of the superconducting surface sheath of type-II and type-I superconductors is reversible, in agreement with theoretical predictions.[2] This agreement is found when the persistent currents around the sample circumference are quenched by plating a strip of chrome parallel to the axis of the cylinder on its surface. The magnetic field H_0 was applied parallel to the cylinder axis. Surface superconductivity is partially or totally suppressed in the plated region, and a singly connected surface superconducting domain is obtained for temperatures between the surface critical temperature $T_3 \equiv T(H_{c3})$ and that of the bulk, $T(H_c)$, for type-I superconductors.

If no plating is performed, the surface that is parallel to the external field H_0 will form a multiply connected superconducting region. Since the surface sheath can sustain finite superconducting currents it is possible that the currents are of such values that the number of fluxoids enclosed in the sample is conserved. If that is the case, the sample is not in the lowest-energy state but in an excited state characterized by the number of fluxoids b.

One obvious way of inducing superconducting surface currents is by changing the external magnetic field. This change is responsible for the absolute value and direction of the induced current. If the fluxoid conservation prevails over the lowest-energy condition, the sample will remain in a giant vortex state. This state is thermodynamically metastable until a critical current is reached. At this current level an irreversible transition will take place, the number of fluxoids will change and the state of the sample will not be characterized by the same quantum number b. This irreversible behavior has been observed experimentally[3,4] and explained theoretically[5,6] using the Ginzburg-Landau equations and imposing fluxoid conservation.

In our experiments an external magnetic field was applied parallel to the axis of a cylindrical sample. The field was kept constant and the temperature was swept through the superconducting transition temperature. Although the condition of fluxoid conservation is still valid it is not obvious how flux conservation can determine the magnetic behavior of the surface sheath when the temperature is the only external variable. The experimental results show that the magnetic flux in the sample changes with temperature and, what is surprising, the variation of flux changes reversibly from a negative (diamagnetic) to a positive (paramagnetic) value when thermally cycled between T_3 and $T(H_c)$. We believe that this behavior is a consequence of fluxoid conservation. The following theoretical analysis, based on the Ginzburg-Landau equations, shows that the main features of the experimental results, presented in Sec. IV, can be explained by the temperature dependence of the giant vortex state.

II. THEORY

Superconductors with Ginzburg-Landau κ values larger than 0.417 have a surface sheath in large magnetic fields. This sheath exists for type-I superconductors for fields between H_c and H_{c3}. The inside of a cylinder, whose radius R is much larger than the coherence length $\xi(T)$, is then in the "normal" state. The surrounding superconducting layer is assumed to have an order parameter

$$\Psi(r,\theta)=\psi(r)\exp(-ib\theta) \quad , \tag{1}$$

which is single valued. The value of b is therefore an integer and is a measure of the fluxoid quantum state of the giant vortex.[5,6]

Our explanation is based on the assumption that the giant vortex settles into a fixed quantum state as it is cooled through H_{c3} in a constant applied field, and that this quantum state is retained over a large temperature range, namely, from T_3 to about $T(H_c)$. As long as the same fluxoid quantum state is maintained, the magnetization changes reversibly with temperature. Near or at H_c the quantum number b changes abruptly, thereby expelling a very large amount of flux from the sample, as the specimen makes a first-order transition to the Meissner state.

With the definitions

$$F(r)=|\Psi|/|\Psi_m|$$

and

$$\vec{Q}=\xi\left(\frac{e^*}{c\hbar}\vec{A}+\vec{\nabla}\Phi\right) \quad ,$$

where $|\Psi_m|$ is the zero-magnetic-field order parameter, $\vec{A}$ is the vector potential, and $\vec{\nabla}\Phi$ is the gradient of the phase of the order parameter, the Ginzburg-Landau (GL) equations are

$$\xi^2\nabla^2F=(F^2+\vec{Q}^2-1)F \quad , \tag{2}$$

$$\lambda^2\nabla\times\nabla\times\vec{Q}=-\vec{Q}F^2=\frac{4\pi}{c}\frac{2\pi\xi\lambda^2}{\phi_0}\vec{j} \quad . \tag{3}$$

λ is the GL penetration depth and $\kappa=\lambda/\xi$. Assuming that the θ component of the vector potential in conventional units is

$$A_\theta=\frac{1}{2}\left(H_0r+H_c\frac{R^2}{r}\varphi(r)\right) \quad , \tag{4}$$

where the function $\varphi(r)$ is to be determined below, it follows that $(Q\equiv Q_\theta)$:

$$Q(r)=\frac{\xi}{r}\left(\frac{\phi_a(r)}{\phi_0}-b+\frac{\Delta\phi(r)}{\phi_0}\right) \quad . \tag{5}$$

Here we have $\phi_a(r)=\pi r^2H_0$ the applied flux over an area of radius r and $\Delta\phi(r)=\pi R^2H_c\varphi(r)$ the excess flux over the same area. From $\nabla\times\vec{A}=\vec{H}$ ($\mu\simeq 1$ is assumed) one obtains for the z component of the local magnetic field

$$H(r)=H_0+H_c\frac{R^2}{2r}\frac{d\varphi}{dr} \quad . \tag{6}$$

Then the change of flux through the cylinder of radius R becomes

$$\Delta\phi=2\pi\int_0^R(H-H_0)r\,dr=\pi R^2H_c\varphi(R) \quad , \tag{7}$$

while the total applied flux to the cylinder is $\phi_a=\pi R^2H_0$.

Equations (2) and (3), when written in cylindrical coordinates (r,θ,z), can be rearranged with the help of Eqs. (5) and (6). One obtains with the definitions $h\equiv H(r)/H_c$ and $h_0\equiv H_0/H_c$

$$\frac{1}{2}r^2\frac{d}{dr}(h^2-h_0^2)=\frac{d}{dr}(r^2Q^2F^2)-\xi^2\frac{d}{dr}\left(r\frac{dF}{dr}\right)^2 - r^2(1-F^2)\frac{dF^2}{dr} \quad . \tag{8}$$

Integrating between $r=0$ and $r=R$, with the boundary conditions

$$\left(\frac{dF}{dr}\right)_{r=0}=0, \quad F(0)=0, \quad (rQF)_{r=0}=0 \quad ,$$

$$H(R)=H_0, \quad \left(\frac{dF}{dr}\right)_{r=R}=0 \quad ,$$

using Eq. (7) and definitions $F(R)\equiv f$, $Q(R)\equiv q$,

$$(\phi_a/\phi_0-b)\xi/R\equiv B$$

and

$$(\Delta\phi/\phi_0)\xi/R\equiv N\xi/R\equiv m \quad ,$$

[N is the number of positive or negative flux quanta in excess of the number of the applied flux quanta ϕ_a/ϕ_0 (within $\pm\frac{1}{2}$)] one obtains

$$\frac{1}{R^2}\left(\int_0^R(h-h_0)^2r\,dr-\int_0^R F^4r\,dr\right)+\frac{2}{R^2}\int_0^R F^2r\,dr+2^{1/2}\frac{2\lambda}{R}h_0m+f^2[(B+m)^2+\tfrac{1}{2}f^2-1]=0 \quad . \tag{9}$$

The first two terms of Eq. (9) are one-half of the normalized Gibbs free-energy difference per unit volume between the normal state and the giant vortex state [Eq. (3) of Ref. 6], that is,

$$\tfrac{1}{2}(G_S-G_N)/(H_c^2V/8\pi)\equiv\tfrac{1}{2}g \quad ,$$

where V is the volume.

Since in the experiments $R>>\xi$ and $F(r)$ is essentially nonzero only near the surface where

$r \simeq R$, the third term in Eq. (9) is related to the thickness of the surface sheath

$$\Delta \equiv \frac{1}{Rf^2} \int_0^R F^2 r\, dr \quad . \tag{10}$$

Therefore Eq. (9) becomes

$$\tfrac{1}{2} g + 2^{1/2} \frac{2\lambda}{R} h_o m + f^2[(B+m)^2 + \tfrac{1}{2} f^2 - 1] + \frac{2\Delta}{R} f^2 = 0 \quad . \tag{11}$$

Consider the free-energy difference g when $R >> \xi$. We may define $\int_0^R F^4 r\, dr \equiv f^4 R \beta \Delta$, where β is of order unity. Furthermore, the first integral in Eq. (9) is always larger than or equal to zero. With the help of Eqs. (3) and (6) this integral is cast into the form below and, as shown in the Appendix, it can be neglected compared to the second term of Eq. (9). Hence ($j \equiv j_\theta$)

$$\tfrac{1}{2} g = \frac{1}{2H_c} \frac{4\pi}{c} \int_0^R \varphi\, j\, dr - \beta \frac{\Delta}{R} f^4 \quad . \tag{12}$$

For $T < T_{c3}$ we expect that $g < 0$ in general, except for possible "superheating" effects when it could become slightly positive. Since the first term in Eq. (12) is always positive the most negative value of g is $-2\beta f^4 \Delta/R$. Therefore, the order of magnitude of $|g|$ is $(\Delta/R) f^4$ or smaller.

We are concerned with materials whose κ values are of order unity and cylinders whose radii are such that Δ/R are of order 10^{-4} for $T < T_c$. Since all the terms in Eq. (11), separately, are of this order of magnitude except the terms $(B+m)^2$, f^2, and unity in the bracket, the sum of all these terms in the bracket must also be of order Δ/R or smaller. We, therefore, write for the bracket $[Q(R) = B + m \equiv q]$

$$q^2 + \tfrac{1}{2} f^2 - 1 = -\frac{\Delta}{R} E \quad , \tag{13}$$

where E is some function of f^2 and m, which must be of order unity or smaller, and which will be estimated below. Defining $t = T/T_c$, $t_3 = T_3/T_c$ and

$$\Delta t = \frac{(t_3 - t)}{(1 - t_3)} \geqslant 0 \quad ,$$

the normalized Gibbs free-energy difference, Eq. (11), is

$$\tfrac{1}{2} g = -\alpha \frac{\xi_3}{R} \frac{N(t)}{(1+\Delta t)^2} - \frac{(2-E)\Delta}{R} f^2(t) \quad , \tag{14}$$

where $\alpha = 6.8 \kappa^2 \xi_3 / R$. The value of $\xi(t_3) \equiv \xi_3$ is a constant and t_3 is defined by the relation

$$H_0 = H_{c3} = 1.7\ (2^{1/2}) \kappa H_c(0)(1 - t_3^2) \quad ,$$

or $h_0 = 1.7\ (2^{1/2}) \kappa / (1 + \Delta t)$ near T_c.

Consider now the "superfluid velocity" Q at the surface of the cylinder. From Eqs. (5) and (13) it follows that:

$$q = \frac{\xi}{R} \left(\frac{\phi_a}{\phi_0} - b + N \right) = \left(1 - \frac{1}{2} f^2 - \frac{\Delta}{R} E \right)^{1/2} \quad . \tag{15}$$

At $\Delta t = 0$ the boundary conditions $f^2 = 0$ and $N = 0$ should apply. Thus the following relation holds:

$$q_3 = \frac{\xi_3}{R} \left(\frac{\phi_a}{\phi_0} - b \right) = \left(1 - \frac{\Delta_3}{R} E_3 \right)^{1/2} \quad , \tag{16}$$

where in our case $\Delta_3 E_3 / R << 1$. Thus the superfluid velocity q_3 at the transition must be finite ($q_3 \simeq 1$) and therefore ϕ_a/ϕ_0 can never be equal to the value of b. This conclusion is consistent with the calculations of Saint-James[7] who calculated the phase boundary between the normal and superconducting states for a small solid cylinder for various quantum states b. In his figure the vertical axis is $(R/\xi)^2 \propto (1-t)$ and the horizontal axis can be labeled as $2\phi_a/\phi_0$. At the phase boundary (ξ_3), that is, at the largest magnetic field at a fixed temperature, the value of ϕ_a/ϕ_0 is always larger than b and obeys approximately the relation $\phi_a/\phi_0 - b \simeq R/\xi_3$ for the larger values of b. It should also be noted that this phase boundary is essentially that measured by Little and Parks[8,9] (on a hollow aluminum cylinder), by Michael and McLachlan[10] on indium cylinders, and by Shablo and Dmitrenko[11] on indium and indium alloy cylinders.

We assume that the value of b is locked-in as the specimen is cooled through the transition in a constant magnetic field, and that this value of b is retained at lower temperatures. The quantity which is measured in our experiments is N which can be readily obtained from Eq. (15) with boundary condition Eq. (16).

$$N = -\left(\frac{\phi_a}{\phi_0} - b \right) + \frac{R}{\xi} q \quad , \tag{17a}$$

or

$$N = \frac{R}{\xi_3} \left\{ \left[(1+\Delta t) \left(1 - \frac{1}{2} f^2 - \frac{\Delta}{R} E \right) \right]^{1/2} - \left(1 - \frac{\Delta_3}{R} E_3 \right)^{1/2} \right\} \quad . \tag{17b}$$

In our case, terms of order $\Delta/R << 1$ can be safely neglected in Eq. (17b) to first approximation, and if $f(t)$ were known, Eq. (17b) would be the desired solution. Equation (17b) shows that N may be zero not only when $f = 0$ at $\Delta t = 0$, but also when $\Delta t > 0$ and $f \neq 0$, that is, when

$$f_0^2 = \frac{2\Delta t_0}{1 + \Delta t_0} \quad . \tag{18}$$

Whether such a "cross-over" point of N exists will depend on the temperature dependence of f when H_0 and b are constant. Since f_0^2 must be smaller or equal to unity, Δt_0 must be bracketed by $0 \leq \Delta t_0 \leq 1$.

It should be noted that Eq. (17a) can be obtained also from the fluxoid quantization relation

$$b\phi_0 = (\phi_a + \Delta\phi) + \frac{4\pi}{c}\lambda^2 \oint \frac{1}{F^2}(\vec{j}\cdot d\vec{s}) \quad , \qquad (19)$$

when evaluated at $r = R$ and use of Eq. (3) is made. Also $q \simeq 1 - \frac{1}{2}f^2$ from Eq. (15), implying that at the transition betwen the normal and superconducting states, the superfluid velocity reaches approximately its maximum value. The supercurrent density, however, approaches zero, because the density of the superelectrons approaches zero $[F^2(r) = 0]$.

Since the observed magnetization is reversible, we believe that the quantum number b is locked-in and uniquely determined at the transition when the temperature is swept at constant magnetic field. We, therefore, have a situation which is akin to the giant vortex state,[5,6] where the magnetization as a function of the applied field was obtained at constant temperature. There it was shown[5,6] that the Gibbs free energy has a minimum at which the magnetization becomes zero $[(\partial G/\partial H_0)_T = -m]$. Adapting this result to the present experiments we may write for Eq. (12)

$$g \simeq -2\beta\frac{\Delta}{R}f^4 \simeq g_0 + A\left[\frac{H_0}{H_{c2}} - \left(\frac{H_0}{H_{c2}}\right)_0\right]^2 + D\left[\frac{H_0}{H_{c2}} - \left(\frac{H_0}{H_{c2}}\right)_0\right]^4 \quad , \qquad (20)$$

where $g = g_0$ is the minimum value of the energy which occurs at $H_0 = H_{c2}(\Delta t_0)$ at which point N changes sign. A and D are constants. Near T_c the value of H_{c2} changes linearly with temperature and, therefore, $H_0/H_{c2} = 1.7/(1+\Delta t)$. If the magnetization increases with infinite slope as the temperature is lowered through t_3, then the value of $D = 0$. If the value of $D \neq 0$ then the magnetization varies linearly with temperature near t_3. Both cases are being considered here.

We shall proceed by discussing the first case $(D = 0)$ in detail and then stating the results of the second case $(D \neq 0)$. Both cases lead to similar results. Since g in Eq. (20) is normalized by $H_c^2(t)$ the minima of g and $G_S - G_N$ as a function of temperature do not coincide. Since $f = 0$ at $\Delta t = 0$ and $f = f_0$ at Δt_0, one obtains from Eq. (20) with Eq. (18),

$$f^4 = f_0^4 \frac{(\beta\Delta)_0}{(\beta\Delta)}\left[1 - \left(\frac{\Delta t_0 - \Delta t}{\Delta t_0(1+\Delta t)}\right)^2\right] \quad . \qquad (21)$$

One would expect that the ratio $(\beta\Delta)_0/\beta\Delta$ is only weakly temperature dependent and we set this ratio equal to unity in what follows.

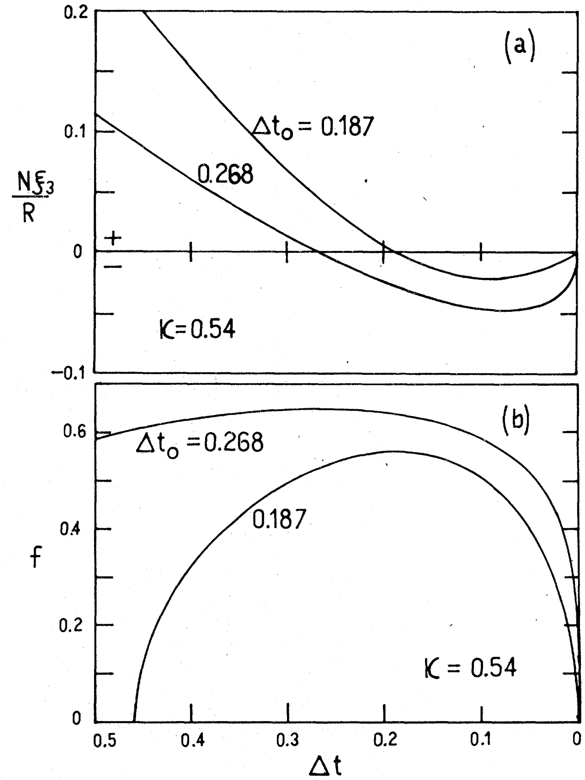

FIG. 1(a). Number of flux quanta N in excess of the number of "applied" flux quanta $\pi R^2 H_0/\phi_0$ is shown as a function of temperature $\Delta t = (t_3 - t)/(1 - t_3)$, where t_3 is the normalized temperature at $H_0 = H_{c3}$ and $\xi_3 = \xi(t_3)$. The curves are calculated from Eq. (22) and apply when H_0 is held constant and the temperature is varied. The curve with the cross-over temperature $\Delta t_0 = 0.187$ is calculated using Eqs. (27) and (29) for $\kappa = 0.54$ and that with $\Delta t_0 = 0.268$ with Eqs. (21) and (25) for the same κ value. For the former result $D \neq 0$ in Eq. (20) for the latter $D = 0$. (b) Order parameters at the surface of the cylinder, corresponding to the solutions of $N(\Delta t)$ in Fig. 1(a), are shown as a function of temperature Δt.

Equation (21) shows that near $\Delta t \simeq 0$ the value of f^2 varies as $(\Delta t)^{1/2}$ and N behaves similarly, as can be checked by substituting f into Eq. (22).

One then finds to a high degree of accuracy the value of N by substituting Eq. (21) into Eq. (17b) and neglecting the terms $\Delta E/R$ and $\Delta_3 E_3/R$ which are certainly very small and of no importance at this point. Results of N and f as a function of Δt are shown in Fig. 1. However, the parameter Δt_0 is still undetermined at this point and we shall find it from the temperature dependence of the function E near $\Delta t \simeq 0$.

E is calculated self-consistently from the energy, that is, from Eqs. (14) and (12) with

$$N\xi_3/R = [(1+\Delta t)(1 - \tfrac{1}{2}f^2)]^{1/2} - 1 \qquad (22)$$

and Eq. (21). This leads to

$$(2-E)\Delta f^2=\beta\Delta f^4-(\alpha R)\frac{\xi_3}{R}\frac{N}{(1+\Delta t)^2} \quad . \quad (23)$$

At $\Delta t=0$ we obtain the value[2] of $\Delta_3=\xi_3$ and we find from Eq. (23) that near $\Delta t\simeq 0$ the temperature dependence is

$$(2-E)\Delta=C_0+C_1(\Delta t)^{1/2} \ ,$$

where C_0 is a constant and C_1 is a function of Δt_0. Since $q_3=1-\Delta_3 E_3/R$ and $q(\Delta t)$ is given by the fluxoid quantization relation, Eq. (17a), we find by matching terms of equal powers of $(\Delta t)^0$, $(\Delta t)^{1/2}$, $(\Delta t)^1$, etc., of Eq. (13) near $\Delta t\simeq 0$ that

$$E_3=2-1.7\kappa^2 \quad (24)$$

and

$$\Delta t_0=\frac{2}{1+4(2\beta-1)/1.7\kappa^2} \quad . \quad (25)$$

The value of E_3 should be interpreted as an "average" value for a fixed value of b in the limit that $\xi_3/R \ll 1$. In this limit we have ignored changes of b which are of order unity and any quasiperiodic properties of E_3. When the magnetic field and the temperature are varied such that the superconducting normal phase boundary is followed[7] and b is constant, the actual value of E_3 varies from a positive to a negative value or vice versa. At the points when b changes by unity, E_3 changes sign and its absolute value.[7] In Eq. (24) the value of κ should be restricted to values such that our assumptions $\lambda/R \ll 1$ and $\xi/R \ll 1$ are not violated.

It follows from Eqs. (24) and (16) that the fluxoid quantum number b is given by

$$b\simeq\frac{1.7}{2}\left(\frac{R}{\xi_3}\right)^2-\frac{R}{\xi_3}+\frac{1}{2}E_3 \ , \quad (26)$$

and is mainly determined by the radius of the cylinder and the coherence length at the transition. The term $\frac{1}{2}(E_3)$ is of no significance in our case, but the term R/ξ_3 is of importance since it is this term which makes q_3 always nonzero. The physical significance of the term R/ξ_3 in Eq. (26) is the following. The current density in the surface sheath is a spatially rapidly varying function over the first coherence length of the surface sheath, measured from the surface,[2,5] over which distance the order parameter $F(r)$ is fairly constant. The current density, Eq. (3), becomes zero at a distance δ from the surface at which point $Q(R-\delta)=0$. The currents to the left and right from this point flow in opposite directions. As shown in the Appendix and Ref. 2, the value of δ near H_{c3}, that is near $\Delta t=0$, approaches $\delta=0.59\xi_3$. Thus we may write $R/\xi_3=2\pi R\,\delta H_{c3}/\phi_0$. Since $2\pi R\,\delta H_{c3}$ is the applied magnetic flux within an area $2\pi R\,\delta$ ($\delta \ll R$), the ratio R/ξ_3 corresponds approximately to the total number of flux quanta, within a distance δ from the surface. These are excluded from the total number of "applied" flux quanta, $\frac{1}{2}[1.7(R/\xi_3)^2]$, in setting the quantum number b of the order parameter at the transition ($\Delta t=0$).

We consider now the case of a second-order phase transition at $\Delta t=0$ for which $D\neq 0$ in Eq. (20). Proceeding similarly as above one finds with f_0^2 given by Eq. (18) and $dg/d\Delta t=0$ at $\Delta t=0$ that

$$f^2=f_0^2\left(\frac{(\beta\Delta)_0}{(\beta\Delta)}\right)^{1/2}\left[1-\left(\frac{\Delta t_0-\Delta t}{\Delta t_0(1+\Delta t)}\right)^2\right] \quad . \quad (27)$$

Near $\Delta t\simeq 0$, f^2 and N are proportional to Δt. Since $dg/d\Delta t=0$ at $\Delta t=0$ for a second-order phase transition, it follows from Eq. (14) with Eqs. (27) and (22) that

$$E_3=2-1.7\kappa^2/2 \ . \quad (28)$$

Substituting the temperature dependences of f^2 and N into Eq. (23) one obtains $(2-E)\Delta=C_0+C_1\Delta t$ near $\Delta t\simeq 0$, where C_1 is a function of Δt_0. Matching terms of equal powers of $(\Delta t)^0$, $(\Delta t)^1$, $(\Delta t)^2$, etc., of Eq. (13) near $\Delta t\simeq 0$ leads to

$$\Delta t_0=\frac{2}{1+8(4\beta-3)/1.7\kappa^2} \quad . \quad (29)$$

Substituting Eq. (28) into Eq. (26) determines the value of b.

The results of the cross-over temperature Δt_0, [Eqs. (25) and (29)], of E_3 [Eqs. (24) and (28)] and of the order parameters [Eqs. (21) and (27)] at the surface of the cylinder are quite similar, when $D=0$ and $D\neq 0$ in Eq. (20). The main difference is that f^2 and N vary as $(\Delta t)^{1/2}$ for $D=0$ and as Δt when $D\neq 0$ near $\Delta t\simeq 0$. Making the term $(\beta\Delta)_0/\beta\Delta\simeq 1$ in Eqs. (21) and (27) may have a slight effect on the accuracy of the results of the cross-over temperature Δt_0 which depends also on β. The latter value is not known exactly except that β should be smaller but close to unity. If the sheath order parameter $F(r)$ were a step function then $\beta=1$; for a Gaussian $\beta=1/2^{1/2}$. Since the sheath is closer to a step function than to a Gaussian we substitute $\beta\simeq 0.9$ into Eq. (29) and find that for $\kappa=0.54$ the value of $\Delta t_0=0.187$. Similarly, one finds from Eq. (25) that $\Delta t_0=0.268$.

Regardless of which solution for f^2 is substituted into Eq. (22), the function $N\xi_3/R$ is a universal function of Δt for a fixed value of Δt_0. Since Δt_0 is not a function of the applied field H_0, and $\xi_3\propto(H_0)^{-1/2}$, the excess flux $N\propto H_0^{1/2}$. Therefore, when N is measured on one specimen for various constant magnetic fields, all values of N must scale as $(H_0)^{1/2}$ (see Figs. 9 and 10).

At $\Delta t=1.7\,(2^{1/2})\kappa-1$ the thermodynamic critical field is reached. At this temperature a transition to the Meissner state will most likely occur. For

$\kappa = 0.54$ this value is $\Delta t = 0.30$. This is above the temperature for which the f^2 functions cease to exist for the above Δt_0 values. A metastable "supercooled" state is possible in this instance but less likely to occur. If Δt_0 would be closer to zero, our solutions of f for a constant b value cease to exist before the Meissner state is reached. In that case the value of b must change at a temperature $\Delta t > 1.7\ (2^{1/2})\kappa - 1$.

Thus when b is locked-in at the transition from the normal to the superconducting state and maintained as the specimen is cooled in a constant magnetic field, the magnetization may reverse sign because of the temperature variation of the order parameter. The latter variation is similar to that of the giant vortex state at constant temperature but varying magnetic field. The following experimental results support this suggestion.

III. EXPERIMENTAL METHODS

The samples used in these experiments were cylinders of $Pb_{99}Tl_{01}$ atomic per cent alloy. The alloy was prepared by melting the components in an inert atmosphere inside a pyrex tube lubricated with a solution of silicon oil in acetone. The samples were annealed a few degrees below the melting temperature for several hours. After annealing, the specimens were chemically polished. When plating was necessary, the sample was first chemically polished, then partially coated with 7031 GE varnish, which was then baked at 100 °C and the uncovered region was electroplated in a chromic acid bath. The electroplated chrome was approximately 10 μm thick.

The samples were thermally anchored to a copper rod that was connected through a thermal resistance to a helium evaporator maintained at constant temperature. The sample temperature was changed by means of a heater wrapped around the upper part of the copper rod. The temperature was determined by a calibrated germanium thermometer connected to the copper rod, below the heater.

The evaporator, the copper rod, and the sample were located inside a vacuum jacket, surrounded by a helium bath at 4 K.

The variation of the magnetic flux at the sample was measured by a SQUID (superconducting-quantum-interference device) magnetometer. The sample was magnetically coupled to the SQUID by a superconducting transformer made with Nb wire. The secondary was placed inside the SQUID and the primary was wound around the vacuum jacket at the center of the sample. The transformer was designed to have a ratio of flux measured at the sample to that seen by the SQUID of approximately 100. The transformer and the SQUID were kept at 4 K. The SQUID was magnetically isolated from the environment by means of a superconducting shield. A magnetic field parallel to the axis of the sample, up to 300 Oe, was applied by a superconducting coil operated in the permanent mode. The ambient magnetic field in the experimental region was reduced to 10^{-2} Oe by proper magnetic shielding.

The magnetic-flux detection system was calibrated by measuring the total explusion of the magnetic flux at the superconducting transition at low fields. Proper precautions were taken to avoid flux trapping in the sample by cooling it in zero applied field well below the transition temperature. Then the field was increased to a constant value and the sample was heated through the transition. This procedure was repeated for various fields. In this way the transformer ratio was found to be 94.

The measurements were done at constant magnetic field while sweeping the temperature. The analogue output of the SQUID was plotted on a x-y recorder as a function of the resistance of the germanium thermometer. The rate at which the temperature was swept was adjusted in such a way that the measured flux variation was time independent.

IV. EXPERIMENTAL RESULTS

All the samples were cylindrical, but the geometry of the surface sheath was of two types. Some experiments were done with a sheath that was singly connected, that is, part of the sheath was suppressed by electrodepositing a strip of chrome on the sample parallel to its axis. This produced a normal region that prevented supercurrents from flowing in the surface sheath around the sample. Other experiments were done without plating; in this case the sheath was multiply connected. Between T_3 and $T(H_c)$ there was a normal core at the center of the cylinder completely enclosed by a superconducting region, around which a net supercurrent could be maintained. The experiments on the partially plated sample were performed in order to determine the superconducting parameters of the samples and for the purpose of comparison with the results of the same sample when multiply connected.

Typical results for a partially plated sample, 5-mm diameter and 26-mm long, are shown in Fig. 2. The change of magnetic flux at the sample expressed in number of flux quanta is plotted as a function of temperature. In this sample the plated region covered 30% of the total surface of the cylinder. It can be seen that the sample became increasingly diamagnetic until a temperature $T(H_c)$ was reached, at which there was an abrupt change in the magnetization, too fast for the SQUID to follow because of its long time constant ($\simeq$1 sec). This change is associated with the explusion of flux when the sample enters the Meissner state. With these $T(H_c)$ we constructed

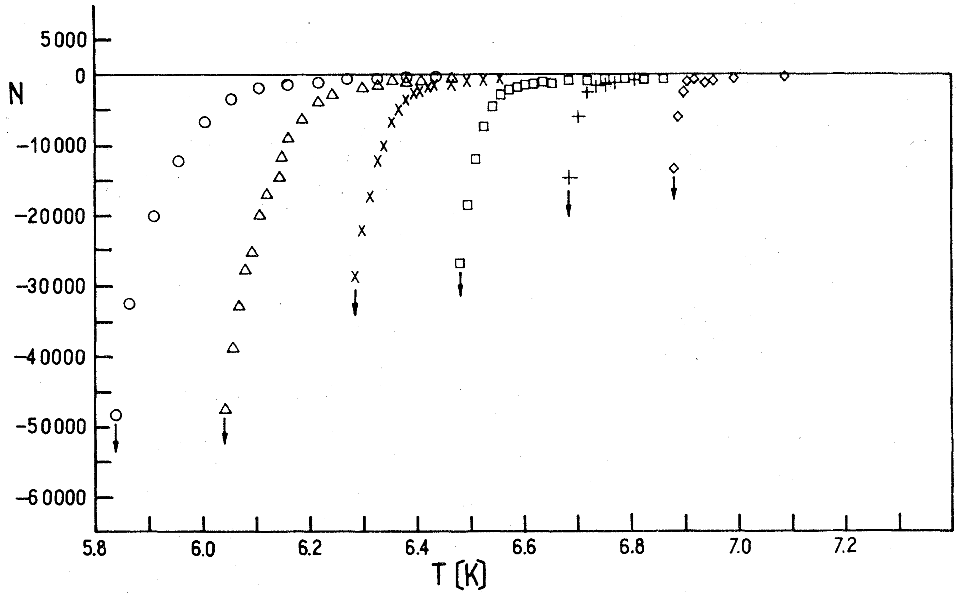

FIG. 2. Change in flux at the sample as a function of temperature for different magnetic fields. A strip of chrome was electrodeposited along the cylinder, making the surface sheath singly connected. Change in flux is plotted in number of flux quanta for fields: ○, 288 Oe; Δ, 240 Oe; ×, 192 Oe; □, 144 Oe; + 96 Oe; ◇, 48 Oe. The arrows indicate the point at which $T(H_c)$ is reached and the SQUID cannot follow the change in flux.

the phase diagram shown in Fig. 3. The experimental points were fitted by least squares to the equation

$$H_c(T) = 866[1-(T/7.098)^2] \ .$$

This agrees within 10% with that reported by Decker *et al.*[12] for pure lead. This shows that this alloy has a Ginsburg-Landau parameter $\kappa < 0.7$ as expected from previous results.[13]

The determination of the surface critical temperature T_3 was not so straightforward because the magnetization shows long diamagnetic tails. When plotting the logarithm of the change in flux as a function of temperature, a change in slope at a well defined temperature is seen in Fig. 4. We define this temperature to be T_3. The resulting phase diagram is shown in Fig. 3. The experimental points are well

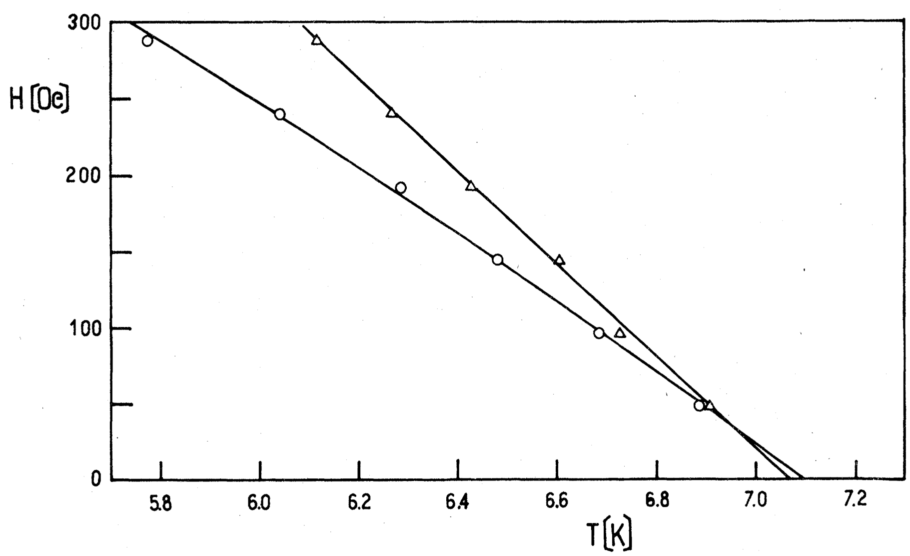

FIG. 3. "Phase diagram" of the $Pb_{99}\,Tl_{01}$ alloy used in our experiments. $T(H_c)$,○, and T_3, Δ, are obtained from our data in the manner described in the text. The surface critical field is fitted by a straight line $H_{c3}(T) = 304(T-7.069)$ and the bulk critical field by a parabola $H_c(T) = 866[1-(T/7.098)^2]$. The corresponding Landau-Ginzburg parameter is $\kappa = 0.52$.

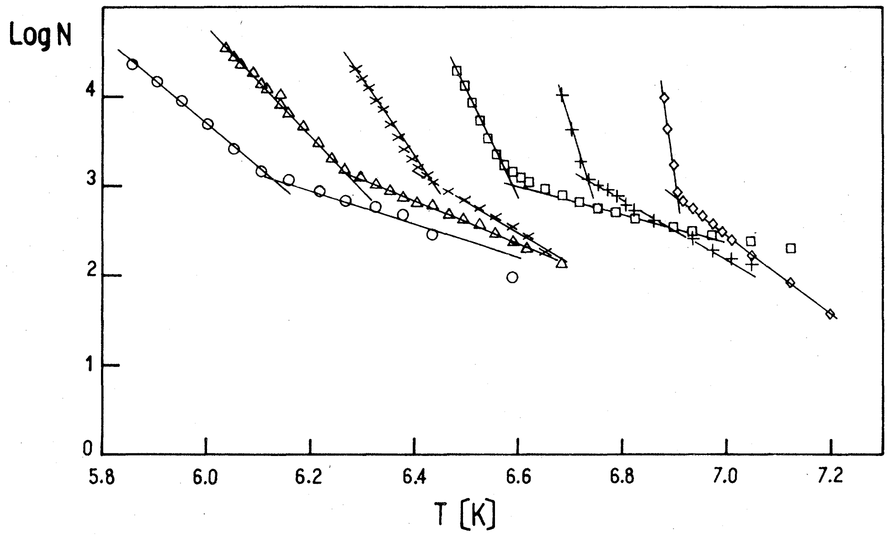

FIG. 4. Logarithm of the change in flux of a sample as a function of temperature for different magnetic fields: ○, 288 Oe; Δ, 240 Oe; ×, 192 Oe; □, 144 Oe; +, 96 Oe; ◇, 48 Oe. The change in slope is associated with T_3.

fitted by $H_{c3}(T)=304(T-7.069)$. Using these values for H_{c3} and H_c we calculate $\kappa=H_{c3}/1.7H_c=0.52$, in agreement with values reported by other authors.[13]

Theoretical[2] and experimental results[1] show a universal behavior when the magnetization and field are plotted in the reduced variables $\mu a(\infty)$ and $H/H_{c2}(T)$. The value of $\mu a(\infty)$ is proportional to the magnetization per unit volume of a sample of dimensions larger than the thickness of the superconducting sheath, H_0 is the applied field, and $H_{c2}=\alpha(T-T_c)$. The curves are universal regardless of the value given to α but only for a unique value of T_c. This value is found to be 7.07 ± 0.01. From our measurement of $H_{c3}(T)$ and $H_{c2}=H_{c3}/1.7$ the value of α is found to be 179 Oe. The value of T_c necessary for a universal plot, as shown in Fig. 5, agrees with that obtained by adjusting $H_c(T)$ and $H_{c3}(T)$ by least squares, and also with the measured T_c at zero field, which is $T_c=7.10\pm0.02$ K. Figure 5 shows the

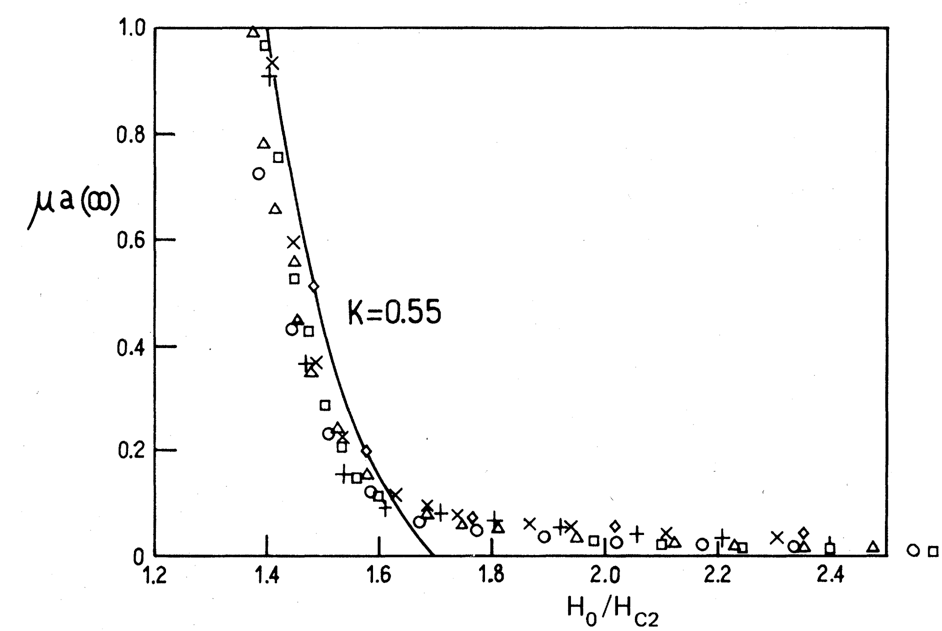

FIG. 5. Results shown in Fig. 2, plotted in the normalized units as used in Ref. 2 as explained in the text, for a semi-infinite half space. The full line represents the theoretical curve for $\kappa=0.55$. Magnetic fields are: ○, 288 Oe; Δ, 240 Oe; ×, 192 Oe; □, 144 Oe; +, 96 Oe; ◇, 48 Oe.

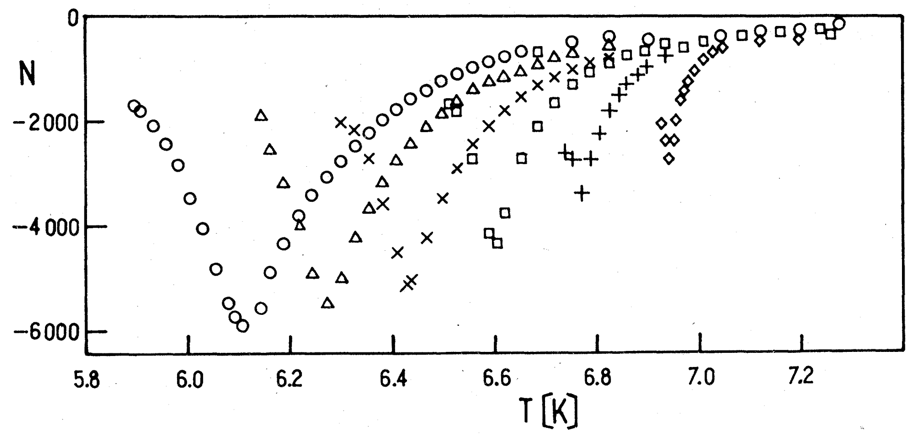

FIG. 6. Change in flux of the sample as a function of temperature in different magnetic fields: ○, 288 Oe; Δ, 240 Oe; ×, 192 Oe; □, 144 Oe; +, 96 Oe; ◇, 48 Oe. The sample is multiply connected. Change in flux is plotted in numbers of flux quanta.

results of Fig. 2 after plotting in reduced variables.

Figures 6 and 7 show the results of two experiments made on the same sample with an unplated surface. The differences between these results and those of Fig. 2 are apparent. One important point is that the results of the partially plated sample are always reproducible, except for minor contributions to the tails of unknown origin above T_3. In the case of unplated samples, the results are not exactly reproducible; they depend on surface conditions in an unknown way. The results shown are from the same sample with the same heat treatment. The bulk critical field and critical temperature coincide in both experiments, in agreement with those of Fig. 3. The difference between the experiments shown in Figs. 6 and 7 is that after completion of the experiment the sample was taken from the cryostat and chemically polished again, using the same procedure as that used in all other experiments. This nonreproducibility after similar surface treatments was also observed in other samples.

Another result is that the diamagnetic tails of the

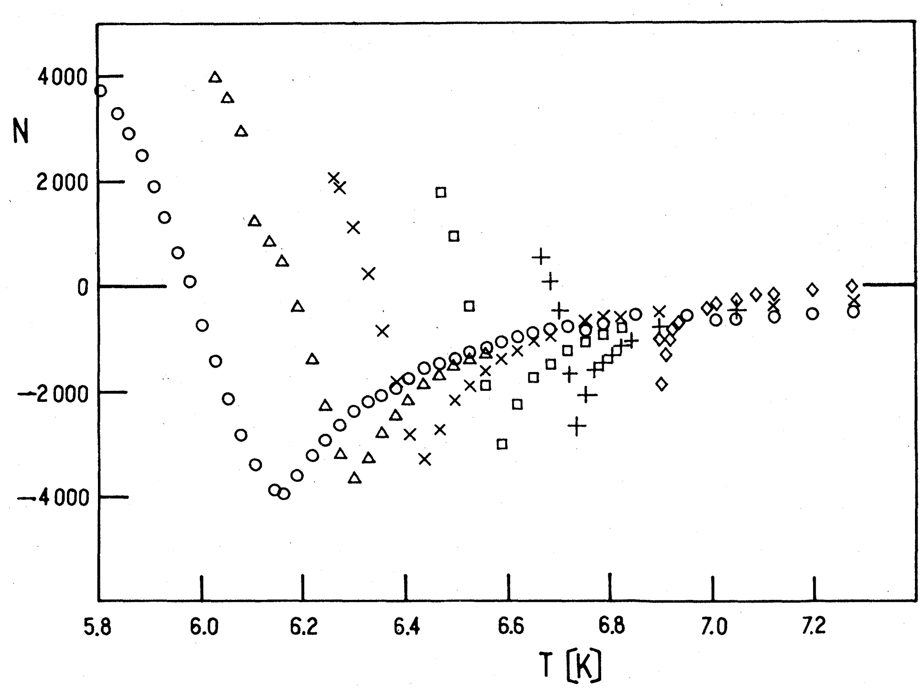

FIG. 7. Change in flux as a function of temperature for different magnetic fields: ○, 288 Oe; Δ, 240 Oe; ×, 192 Oe; □, 144 Oe; +, 96 Oe; ◇, 48 Oe. The sample was multiply connected as it was the case in Fig. 6 and the only difference was in the surface treatment, as explained in the text.

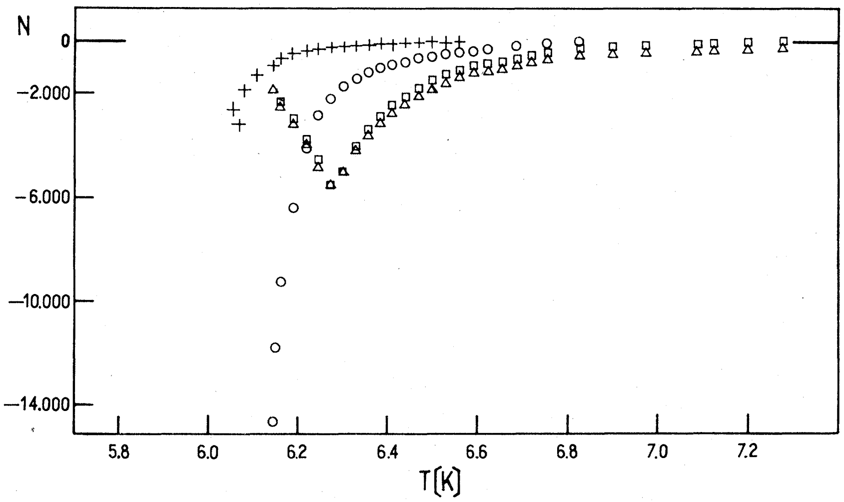

FIG. 8. Comparison of the magnetization as a function of temperature for different sample conditions. Magnetic field is 240 Oe for all the curves shown. ○, Partially plated sample—Singly connected surface sheath. +, Completely plated sample—Partially suppressed surface sheath. □, Unplated sample—Multiply connected sheath. The temperature was *decreased* from above T_3. Δ, Unplated sample—The temperature was *increased* from a value slightly higher than $T(H_c)$.

unplated specimens above T_3 are larger than those of the plated (singly connected) samples. In Fig. 8 we show the results, measured in a field of 240 Oe, of an unplated, a partially plated, and a completely plated sample. Until now we have not been able to control the surface treatment in such a way as to obtain quantitatively reproducible results.

The following describes what we believe is characteristic of a fluxoid quantum state. It can be seen in Figs. 6 and 7 that the multiply connected samples show an increase of the diamagnetic magnetization above T_3 when the temperature is decreased until a maximum near T_3 is reached. The diamagnetism then decreases towards zero magnetic moment and eventually it becomes paramagnetic, before the diamagnetic bulk transition at $T(H_c)$ takes place. The change in sign of the slope of the magnetization is a general characteristic of the magnetic response of the multiply connected samples when the temperature is swept at constant magnetic field. This behavior was verified by several experiments after repolishing the surface of the sample. All the experiments had in common: (a) the inversion of the slope of the magnetization, and (b) a nearly linear decrease of the diamagnetism below T_3.

Similar behavior was also found for samples of the same alloy whose diameters were 2 mm.

In order to detect if our results were due to currents induced by possible thermal gradients in the sample, produced by heat losses, the heater at the copper rod was switched off and the thermal sweep was accomplished by applying heat through the sample at the opposite end. The results obtained in this way were the same as the ones previously obtained with the heater in the copper rod. Since the temperature gradient established in the sample was much larger than that produced by any thermal loss, it was concluded that the induced currents had no origin in thermal gradients. From the measured thermal conductivity of this alloy and the known applied heat flux it was determined that the maximum temperature difference in the sample was a few millidegrees; this explains why the magnetization curves were not different from the ones taken at uniform temperature.

V. DISCUSSION

Studying the fluctuation-induced diamagnetism in type-II superconductors, Gollub *et al.*[14] reported a change in the slope of the magnetization at T_3, similar to the one found here. They proposed no explanation for their observations. Since they were interested in measuring the bulk-induced diamagnetism, they plated the surface of the sample with a normal metal and made no further detailed study of the aforementioned observations. Up to now we have not considered in our discussion contributions of the fluctuation-induced diamagnetism to the total variation of magnetic flux. The tails above $T_c(H)$ in the totally plated samples are of the same order of magnitude as those measured[14] for similar alloys. The low sensitivity of our transformer does not allow for a detailed comparison with those results.

Knowing that our alloy is a type-I superconductor and using the results of Ref. 14, we conclude that the fluctuation-induced diamagnetism is small when compared to the values of the magnetization obtained for the giant vortex state. However the possible contri-

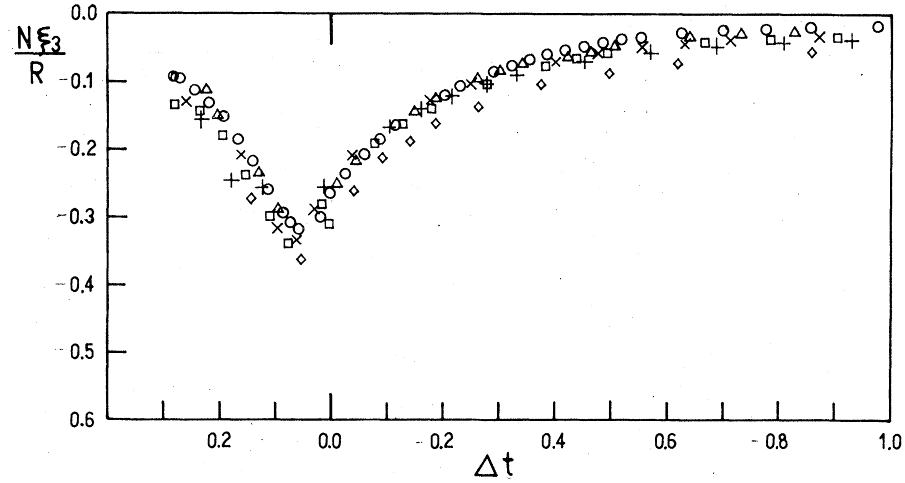

FIG. 9. Change in flux times $\xi_3/R\,\phi_0$ as a function of Δt. The reduced variables are defined in Sec. II. The points correspond to those plotted in Fig. 6: ○, 288 Oe; Δ, 240 Oe; ×, 192 Oe; □, 144 Oe; + 96 Oe; ◇, 48 Oe. The diamagnetic tails above T_3 (i.e., $\Delta t < 0$) also superimpose when plotted in reduced variables.

bution of the fluctuations to the induced sheath currents on the surface sheath is not known.

The enhancement of the values of the tails above T_3 in the unplated samples is not due to bulk fluctuations because the enhancement is reduced when partially plating the surface of the samples.

In a constant magnetic field, the magnetization of the Meissner state varies only very slightly with temperature due to the temperature dependence of the penetration depth. The shielding current flows in one direction only, and the magnetization does not reverse sign. In the surface sheath state the magnetization may reverse sign, however, because there are two surface currents of large magnitudes, flowing in opposite direction. Due to a change in field or temperature, an imbalance of these currents may cause the net current to be in either direction. It is therefore reasonable to expect different temperature dependences of the magnetization in a constant field for the Meissner and surface sheath states when the fluxoid quantum number is conserved.

Before comparing the experimental results with the theory of the temperature dependence of the giant vortex state, let us analyze some of the experimental facts that induced us to believe that they are the manifestation of a temperature dependent quantized macroscopic superconducting state. First of all it is very difficult to think "classically" of a mechanism that could induce currents in opposite directions when temperature is the only external variable. If fluxoid conservation is imposed instead of minimum energy, the direction and magnitude of the current will be adjusted by the quantum state which has been locked in the sample. One characteristic of this quan-

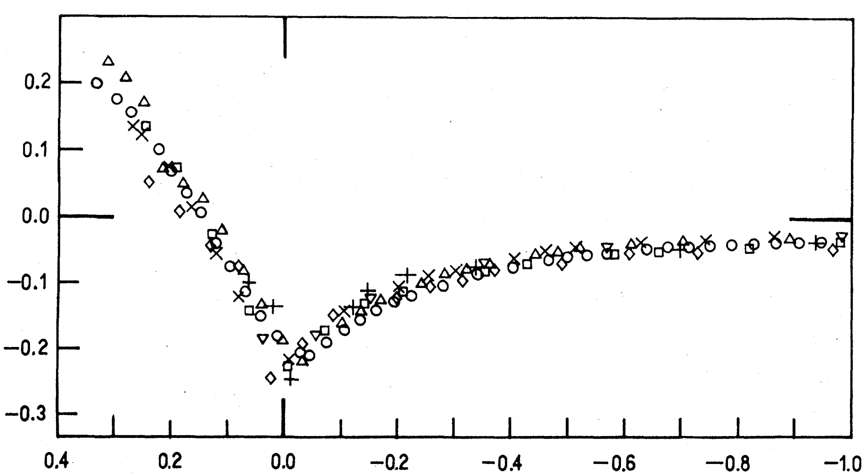

FIG. 10. Change in flux reduced variables as in Fig. 9. The points correspond to those of Fig. 7: ○, 288 Oe; Δ, 240 Oe; ×, 192 Oe; □, 144 Oe; +, 96 Oe; ◇, 48 Oe.

tum state is that the magnetization should behave reversibly, as long as the state is characterized by the same number of fluxoid quanta. If by sweeping temperature there is a change in the number of quanta the variation of magnetic flux should be irreversible. Figure 8 shows the reversible variation of flux as a function of temperature, at a constant magnetic field of 240 Oe, when the temperature is increased and decreased. On the other hand if the temperature is swept below $T(H_c)$ and then increased above this value the resulting flux variation is completely irreversible. The flux jumps are so large and fast that the SQUID cannot follow them, unitl temperatures near T_3 are reached. The expulsion of flux from the bulk of the sample at $T(H_c)$ induces critical currents. An increase in temperature reduces the critical current, thereby maintaining the critical surface state. This means that the surface is not able to conserve the fluxoid number and transitions to different quantum states take place. Results for other fields and samples have similar behavior but are not plotted for clarity. We see that these experimental facts support the idea of a locked quantum state as discussed in Sec. II. This is not the only evidence of fluxoid conservation. It was shown in Sec. II that the inversion of the slope and sign of the magnetization, as indicated by Eqs. (25) and (29), are characteristic of the temperature dependence of the vortex state, as observed experimentally. It is also indicated in Sec. II and shown by Eq. (22) that the variation of flux as a function of temperature should be a universal function, when the change in flux is multiplied by $\xi_3/R\,\phi_0$ and the temperature expressed in the form $(t-t_3)/(t_3-1)$. In Figs. 9 and 10 we show the results of such a normalization for the experimental results of Figs. 6 and 7. The excellent superposition of all curves can be seen. In these graphs t_3 is determined from the experimental values of $H_{c3}(t)$, as shown in Fig. 3. We see that the universality and the order of magnitude of the change in flux are in agreement with the predictions of the theory, Fig. 1. On the other hand, exact quantitative agreement cannot be expected until the influence of the surface preparation is fully understood. The latter determines the quantum number b which the sample locks-in at T_3. It is seen from our results that the surface of the sample is capable of sustaining induced supercurrents above T_3, where T_3 is obtained from the partially plated sample. It is possible to think of a thinner surface superconducting "sheath" of a higher κ value, in the outermost part of the cylinder. This thin layer would give a small contribution to the magnetization for the partially plated samples due to the larger κ value, but when multiply connected, it could lock the fluxoid number above T_3. The experimental results could be a superposition of two curves, one arising from the larger κ value with a Δt_0 much larger than the one for $\kappa=0.52$.

In conclusion we are able to explain the reversible change in sign of the magnetization of a superconducting cylinder in a constant applied (axial) magnetic field, when thermally cycled between $T(H_{c3})$ and $T(H_c)$, by the concept of the giant vortex state.

ACKNOWLEDGMENTS

This research was supported in part by OAS Multinational Program of Physics and by NSF Grant GF 38710. We wish to thank the S.H.E. Corportation, San Diego, California, for their advice and the Low Temperature Group at Bariloche for helpful discussions.

APPENDIX

We show that the first term on the right-hand side of Eq. (12) is much smaller than the second term. Consider the integral I,

$$I \equiv \frac{1}{R^2}\int_0^R (h-h_0)^2 r\,dr = \frac{1}{2H_c}\frac{4\pi}{c}\int_0^R \phi(r) j(r)\,dr > 0 \ . \tag{A1}$$

We know from the exact solutions of the giant vortex[5] that $\varphi(r)$ is a spatially slowly varying function over the first coherence length from the surface (boundary condition $d\varphi/dr=0$ at $r=R$) (Ref. 5, Fig. 4). However $j(r)\propto -Q(r)F^2(r)$ changes very rapidly over this distance. From Eq. (5) it follows that $Q(r)=0$ at $r=R-\delta$, where the distance δ from the surface is

$$\frac{\delta}{\xi_3}=\frac{0.59}{1+\Delta t}\left[1+\frac{\varphi(R-\delta)}{\varphi(R)}\left(\frac{\xi_3}{R}N\right)\right] \ . \tag{A2}$$

At $\Delta t=0$ the last term of Eq. (A2) is zero. In that limit $\delta=0.59\xi_3$. Generally $\phi(R-\delta)/\phi(R)\simeq 1$, and in our case $|N\xi_3/R|\leq 0.2$, so that the distance from the surface at which $j(r)=0$ varies from $0.59\xi_3$ to about $0.50\xi_3$ (at most), and $Q(R)$ from unity to about 0.9 (at most), in our case. Therefore Eq. (A1) is approximately

$$I \simeq \frac{\varphi(R)}{2H_c}\frac{4\pi}{c}\int_0^R j(r)\,dr \simeq \tfrac{1}{2}\varphi(R)\frac{H_{\rm sol}-H_0}{H_c} \ , \tag{A3}$$

where $H_{\rm sol}$ is the uniform field inside a solenoid of radius R and of wall thickness $\Delta \ll R$, generated by a current per unit length $\int_0^R j(r)\,dr$.

Here we may apply the results derived from the surface sheath on a semi-infinite half space with different applied fields on each side of the sheath.[15]

This, with $H_\infty \equiv H_{sol}$, is approximately

$$\frac{H_{sol}^2 - H_0^2}{2H_c^2} \simeq f^2(1 - q^2 - \tfrac{1}{2}f^2) = \frac{\Delta E f^2}{R} . \quad \text{(A4)}$$

Because $H_{sol} + H_0 \simeq 2H_0$, Eq. (A3) can be expressed in terms of $\Delta f^2/R$, and when Eq. (A.3) is then substituted into Eq. (12) one obtains

$$\tfrac{1}{2}g \simeq \frac{\Delta}{R} f^2 \left[\frac{\xi_3}{R} \left(\frac{\xi_3}{R} |N| \right) \frac{|E|}{1.7} - \beta f^2 \right] . \quad \text{(A5)}$$

$|E|/1.7$ is of order unity, $|N|\xi_3/R \lesssim 0.2$ and $\xi_3/R < 10^{-4}$ in our case. Also $N \propto f^2$ near $\Delta t \simeq 0$. Thus the first term on the right-hand side of Eq. (A.5) is always very much smaller than the second, except perhaps when $f^2 \to 0$ for $\Delta t < \Delta t_0$. This temperature is, in our case, below that at which the transition to the Meissner state occurs. Checking the numerical results of Refs. 5 and 6 reveals that for dimensions of $R/\xi \sim 3-5$ this term is also of no importance as far as the total Gibbs free-energy Eq. (12) is concerned.

---

*On leave from the Department of Electrical Engineering, University of California, Davis, Calif. 95616.
†Comisión Nacional de Energía Atómica.
‡Universidad Nacional de Cuyo.

[1] J. Luzuriaga and F. de la Cruz, Solid State Commun. 25, 605 (1978).
[2] H. J. Fink and R. D. Kessinger, Phys. Rev. A 140, 1937 (1965).
[3] L. J. Barnes and H. J. Fink, Phys. Rev. 149, 186 (1966).
[4] L. J. Barnes and H. J. Fink, Phys. Lett. 20, 583 (1966).
[5] H. J. Fink and A. G. Presson, Phys. Rev. 151, 219 (1966).
[6] H. J. Fink and A. G. Presson, Phys. Rev. 168, 399 (1968).
[7] D. Saint-James, Phys. Lett. 15, 13-14 (1965).
[8] W. A. Little and R. D. Parks, Phys. Rev. Lett. 9, 9 (1962); Phys. Rev. 133, A97 (1964).
[9] R. P. Groff and R. D. Parks, Phys. Rev. 176, 567 (1968).
[10] P. Michael and D. S. McLachlan, J. Low Temp. Phys. 14, 607 (1974).
[11] A. A. Shablo and I. M. Dmitrenko, *Proceedings of the 12th International Conference on Low Temperature Physics* (Academic, Japan, 1971), p. 407.
[12] D. L. Decker, D. E. Mapother, and R. W. Shaw, Phys. Rev. 112, 1888 (1958).
[13] G. Bon Mardion, B. B. Goodman, and A. Lacaze, J. Phys. Chem. Solids 26, 1143 (1965).
[14] J. P. Gollub, M. R. Beasley, R. Callarotti, and M. Tinkham, Phys. Rev. B 7, 3039 (1973).
[15] H. J. Fink and A. G. Presson, Phys. Rev. B 1, 1091 (1970).