PHYSICAL REVIEW VOLUME 132, NUMBER 2 15 OCTOBER 1963

Properties of a Thin Hollow Superconducting Cylinder

D. H. DOUGLASS, JR.*
Department of Physics and Institute for the Study of Metals, University of Chicago, Chicago, Illinois
(Received 14 June 1963)

The properties of a thin, superconducting cylindrical tube are considered by means of the Ginsburg-Landau theory. The equations have been solved under the condition that the magnitude of the energy gap (order parameter) is independent of position but not independent of magnetic field H_0 or of fluxoid quantum number n. This latter dependence on H_0 and n, which is usually ignored, is found to lead to modification of the expressions for the various superconducting properties. In the limit $rd/\lambda^2 \leq 1$, where r is the radius, d the thickness, and λ the penetration depth, the energy gap goes smoothly to zero with magnetic field for a fixed n, defining a second-order phase transition. The magnetization, the current density, and the free energy also go smoothly to zero, with the curves for different n being displaced by n times the field corresponding to unit quantum. For this case the transition temperature is periodic with magnetic field with period corresponding to unit quantum, which agree with the experiments of Little and Parks and the calculation of Tinkham. In the limit $rd \geq \lambda^2$, the energy gap drops discontinuously to zero at critical conditions, giving a first-order phase transition, with a corresponding influence on the other properties of the superconductor; also the possibility of a thermodynamically metastable region with respect to the normal state arises. In order to obtain agreement with the measurements of critical persistent currents and the measurements of flux quantization, it must be assumed that n is a good quantum number under any conditions as long as the system remains superconducting. This leads to metastable states which for the $rd \geq \lambda^2$ case includes states which are thermodynamically metastable as well.

I. INTRODUCTION

THE subject of flux (or fluxoid) quantization in superconductors has received a great deal of interest recently. Following the theoretical predictions of quantization by London[1] and Onsager,[2] Deaver and Fairbank[3] and Doll and Näbauer[4] showed experimentally that the trapped flux of a hollow superconducting cylinder was indeed quantized. These experimental results generated a spate of theoretical activity concerning the various properties of the hollow cylinder.[5–18]

With the exception of the work of Tinkham,[18] these investigations have not considered that the energy gap depends on the external field H_0 and the fluxoid quantum number n; because all the various properties depend on the energy gap, modification of the expressions for these quantities is necessary. Additional questions arise concerning under what conditions good quantum numbers can be found, and once found how is it possible with an external perturbation to change the system from one quantum state to another. This paper considers these questions.

The dependence of the energy gap on n and H_0 and its influence on the other properties of the hollow cylinder are considered in a self-consistent manner via the Ginzburg-Landau[19] (GL) theory.[20] The calculation has been done under the condition that the magnitude of the order parameter Ψ (energy gap) is independent of position (but not of H_0 and n), which is equivalent to the condition that the thickness of wall be less than the coherence length. In this approximation, it is shown in Sec. IIA that the energy-gap, the free-energy, and the transition-temperature curves as functions of magnetic field consist of a set of intersecting "parabolas," each one corresponding to a particular n. These "parabolas" are displaced by the field associated with the unit quantum, and their vertices lie on an envelope curve

* Alfred P. Sloan Fellow.
[1] F. London, *Superfluids* (John Wiley & Sons, Inc., New York, 1950), p. 152.
[2] L. Onsager, in *Proceedings of the International Conference of Theoretical Physics, Kyoto and Tokyo, 1953* (Science Council of Japan, Tokyo, 1954) pp. 935–936. The possibility of the effective charge being twice the electronic charge was mentioned to W. Fairbank in a private communication. (See footnote 3 of Ref. 3.) Also Phys. Rev. Letters **7**, 50 (1961).
[3] B. S. Deaver, Jr., and W. M. Fairbank, Phys. Rev. Letters **7**, 43 (1961).
[4] R. Doll and M. Näbauer, Phys. Rev. Letters **7**, 51 (1961).
[5] N. Byers and C. N. Yang, Phys. Rev. Letters, **7**, 46 (1961).
[6] J. M. Blatt, Phys. Rev. Letters **7**, 82 (1961); Progr. Theoret. Phys. (Kyoto) **26**, 761 (1961).
[7] John Bardeen, Phys. Rev. Letters **7**, 162 (1961).
[8] J. B. Keller and B. Zumino, Phys. Rev. Letters **7**, 164 (1961).
[9] W. Brenig, Phys. Rev. Letters **7**, 337 (1961).
[10] A. Bohr and B. R. Mottelson, Phys. Rev. **125**, 495 (1962).
[11] K. Maki and T. Tsuneto, Prog. Theoret. Phys. (Kyoto) **27**, 228 (1962).
[12] G. Luders, Z. Naturforsch. **17a**, 181 (1962).
[13] W. Weller, Z. Naturforsch. **17a**, 182 (1962).
[14] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **42**, 299 (1962) [translation: Soviet Phys.—JETP **15**, 207 (1962)].
[15] H. Lipkin, M. Peshkin, and L. Tassie, Phys. Rev. **126**, 116 (1962).
[16] M. Peshkin and W. Tobocman, Phys. Rev. **127**, 1865 (1962).
[17] F. Bloch and H. Rorschach, Phys. Rev. **128**, 1697 (1962).
[18] M. Tinkham, Phys. Rev. **129**, 2413 (1963).
[19] V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. **20**, 1064 (1950).
[20] It is of historical interest to note that flux quantization was contained implicitly in the GL theory at its inception (1950). Had a calculation for the hollow cylinder been performed, the single-value requirement on the order parameter Ψ would have yielded quantization immediately; in addition, the magnitude would have been given correctly if the effective charge in the theory had been taken as $2e$ as certain experiments suggested. In a later paper A. A. Abrikosov {Zh. Eksperim. i Teor. Fiz. **32**, 1442 (1957) [translation: Soviet Phys.—JETP **5**, 1174 (1957)]} used the GL theory in a calculation of the magnetization of a superconductor of the "second kind"; he found a "vortex" type of solution for Ψ for which the flux through each "vortex" was quantized.

which is quadratic in H_0 for small H_0. The magnetization shows a similar periodicity.

A consideration of the microscopic state of the system leads one to conclude that cylindrical symmetry is not essential to obtaining good quantum numbers; in fact, the only requirements for a doubly connected system is single valuedness of Ψ. A calculation presented in Sec. IIB for a composite hollow cylinder consisting of two different superconductors agrees with this conclusion.

A further consideration of the nature of the microscopic state leads to the very plausible assumption that changes in an external magnetic field are adiabatic, i.e., processes in which the quantum number n remains constant. This statement turns out to be equivalent to London's hypothesis of "stiff wave functions," in which the "canonical momentum" is invarient under a change in magnetic field. This means that a change of the magnetic field does not induce transitions to states of lower energy unless the system is first brought into the normal state. Comparison of experimental results with the calculations in Sec. IIA shows this to be correct, even in regions of thermodynamic metastability.

II. SOLUTION OF THE GL EQUATIONS FOR A THIN HOLLOW SUPERCONDUCTING CYLINDER

A. Homogeneous Hollow Cylinder

Self-Consistent Solutions for $\mathbf{A}$ *and* Ψ *Assuming* $|\Psi|$ *Independent of Position*

In the GL theory the order parameter Ψ which can vary with position and magnetic field is related to the vector potential $\mathbf{A}$ through a pair of coupled nonlinear differential equations. For a cylinder of arbitrary cross section with an external field H_0 parallel to the axis, the GL equations can be expressed in the form[19]

$$\left(\nabla+\frac{ie^*}{\hbar c}\mathbf{A}\right)^2\psi+\frac{\kappa^2}{\lambda^2}(1-|\psi|^2)\psi=0, \tag{1}$$

$$\nabla\times\nabla\times\mathbf{A}=\frac{i\hbar c}{2e^*\lambda^2}(\psi^*\nabla\psi-\psi\nabla\psi^*)-\frac{|\psi|^2}{\lambda^2}\mathbf{A}, \tag{2}$$

with boundary conditions given by

$$(i\hbar\nabla\psi+(e^*/c)\psi\mathbf{A})_\perp=0 \quad \text{on both surfaces}, \tag{3}$$

$$\nabla\times\mathbf{A}=\mathbf{H}_0 \quad \text{on outer surface}, \tag{4a}$$

$$\nabla\times\mathbf{A}=2\mathbf{A}/r \quad \text{on inner surface},^{21} \tag{4b}$$

where $\psi=\Psi(T,A)/\Psi(T,0)$, $e^*=2e$ is the charge of a "Cooper pair."[22] The penetration depth λ and the dimensionless coupling constant κ are given by[23]

$$\lambda^2=\frac{\lambda_L^2}{\chi}=\frac{mc^2}{4\pi e^{*2}|\psi(T,0)|^2\chi}, \tag{5}$$

$$\kappa=\frac{\kappa_0}{\chi}=\frac{\sqrt{2}e^*\lambda_L^2H_{cb}}{\hbar c\chi}=\frac{\sqrt{2}e^*\lambda^2H_{cb}}{\hbar c}, \tag{6}$$

where H_{cb} is the bulk critical field and χ is a function of the ratio of the bulk coherence length ξ_0 to the electronic mean free path l; χ can be approximated[24] within an accuracy of about 20% by $\chi=(1+\xi_0/l)^{-1}$.

Once the equations above are solved, the properties of the superconductor can be readily determined in terms of $\mathbf{A}$ and ψ. The solution of these equations for the multiply connected cylinder has been considered by a number of investigators[7,8,12,14] but with the approximation $|\psi|=1$; this restricts their solutions to weak fields and small quantum numbers. For later reference some of these expressions are written here: the magnetic Gibbs free energy,

$$\mathcal{G}_{SH}=\mathcal{G}_{NH}+\frac{H_{cb}^2}{8\pi}\int_{\text{Superconductor}}d^3r\left\{|\psi|^4-2|\psi|^2+\frac{2\lambda^2}{\kappa^2}\left|\nabla\psi+\frac{ie^*}{\hbar c}\psi\mathbf{A}\right|^2\right\}+\frac{1}{8\pi}\int_{\text{all space}}d^3r[\mathbf{H}(\mathbf{r})-\mathbf{H}_0]^2; \tag{7}$$

the magnetic moment,

$$\mathfrak{M}=\frac{1}{4\pi}\int_{\text{all space}}d^3r[\mathbf{H}(\mathbf{r})-\mathbf{H}_0]; \tag{8}$$

the current density $\mathbf{J}$ as given from Maxwell equations,

$$\frac{4\pi}{c}\mathbf{J}=\nabla\times\nabla\times\mathbf{A}, \tag{9}$$

which with the use of (2) can be written

$$\frac{4\pi}{c}\mathbf{J}=\frac{i\hbar c}{2e^*\lambda^2}(\psi^*\nabla\psi-\psi\nabla\psi^*)-\frac{|\psi|^2}{\lambda^2}\mathbf{A}. \tag{10}$$

It is worth pointing out here that if the first two terms on the right-hand side of (10) were not there, one obtains the London relationship between the current and the vector potential.[25] In a multiply connected sample, however, these terms cannot be set equal to zero and will be shown to be a function of the fluxoid

[21] This comes from the assumption that the flux across the boundary is continuous plus the fact that the field in the hole is constant with position.

[22] L. N. Cooper, Phys. Rev. **104**, 1189 (1956).

[23] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **37**, 1407 (1959) [translation: Soviet Phys.—JETP **10**, 998 (1959)].

[24] D. H. Douglass, Jr., Phys. Rev. **124**, 735 (1961).

[25] This is not strictly true because here $|\psi|^2$ is a function of $\mathbf{A}$ whereas the London theory implicitly assumes $|\psi|^2=1$.

quantum number; thus the current consists of a quantized part and a diamagnetic part.

Equations (1) and (2) will now be solved for a hollow circular cylinder of inner radius r_1 and wall thickness d in an external magnetic field H_0 as illustrated in Fig. 1. The reduced order parameter ψ can be written as

$$\psi=\phi e^{-i\eta}, \tag{11}$$

where ϕ is the magnitude and η the phase. In this section it is assumed that ϕ does not vary with position; this approximation can be made without too great an error as long as d is less than the coherence length ξ, which is the characteristic distance over which ϕ changes.[26] No assumption need be made concerning whether d is greater or less than λ, which is the characteristic distance over which $\mathbf{A}$ changes. Taking advantage of the cylindrical symmetry, it is further assumed that: $\mathbf{H}$ is everywhere in the z direction and a function only of r, which implies that $\mathbf{A}$ and $\mathbf{J}$ are only in the θ direction and are also only functions of r; $\partial/\partial z=0$; and $\nabla\cdot\mathbf{A}=0$. With these assumptions Eq. (2) becomes

$$\frac{d}{dr}\left[\frac{1}{r}\frac{d}{dr}(rA)\right]=\frac{\phi^2}{\lambda^2}\left(-\frac{\hbar c}{e^*r}\frac{\partial\eta}{\partial\theta}+A\right). \tag{12}$$

Because the left-hand side of (12) and the term in A on the right-hand side are functions only of r so must the remaining term be, which requires that

$$\frac{\partial\eta}{\partial\theta}=f(r), \tag{13}$$

or

$$\eta=f(r)\theta+g(r). \tag{14}$$

Assuming no radial currents, g can at most be a constant representing an arbitrary and meaningless phase which can be chosen equal to zero. The requirement that ψ be single valued

$$\psi(\theta)=\psi(\theta+2\pi) \tag{15}$$

leads to

$$f=n;\quad n=\text{integer}. \tag{16}$$

Thus, the order parameter becomes

$$\psi(\theta)=\phi e^{-in\theta}, \tag{17}$$

and (12) reduces to

$$\frac{d}{dr}\left[\frac{1}{r}\frac{d}{dr}(rA)\right]=\frac{\phi^2}{\lambda^2}\left(A-\frac{\hbar cn}{e^*r}\right). \tag{18}$$

The substitution $A'=A-\hbar cn/e^*r$ results in Bessel's equation for A', whose integration yields

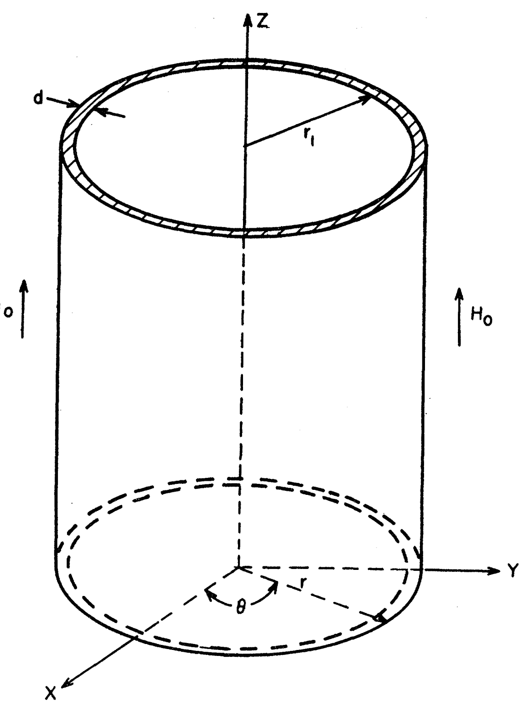

FIG. 1. Hollow cylindrical tube.

$$A(r)=C_1I_1\left(\frac{r\phi}{\lambda}\right)+C_2K_1\left(\frac{r\phi}{\lambda}\right)+\frac{\hbar cn}{e^*r}, \tag{19}$$

where I and K are the modified Bessel functions of the first kind.[27] The integration constants C_1 and C_2 are determined from the boundary conditions (4a) and (4b):

$$C_1=\left([K_1(\alpha)+\tfrac{1}{2}\alpha K_0(\alpha)]\frac{H_0\lambda}{\phi}-K_0(\beta)\frac{\hbar cn}{e^*r_1}\right)\Big/\times\Delta(\alpha,\beta), \tag{20}$$

$$C_2=\left([\tfrac{1}{2}\alpha I_0(\alpha)-I_1(\alpha)]\frac{H_0\lambda}{\phi}-I_0(\beta)\frac{\hbar cn}{e^*r}\right)\Big/\Delta(\alpha,\beta), \tag{21}$$

where

$$\Delta(\alpha,\beta)=I_0(\beta)[K_1(\alpha)+\tfrac{1}{2}\alpha K_0(\alpha)]+K_0(\beta)[I_1(\alpha)-\tfrac{1}{2}\alpha I_0(\alpha)], \tag{22}$$

$$\alpha=(r_1\phi)/d, \tag{23}$$

$$\beta=(r_1+d)(\phi/d). \tag{24}$$

[26] More precisely the characteristic distance in the GL theory describing changes in $|\psi|^2$ is λ/κ, but Gor'kov (see Ref. 23) has shown that $\xi\approx\lambda/\kappa$.

[27] See A. Erdélyi, W. Magnus, F. Iberhettinger, and F. Tricomi, *Higher Transcendental Functions*, (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 2, p. 9.

The magnetic field is given by curl $\mathbf{A}$ and is

$$H(r)=\frac{\phi}{\lambda}[C_1I_0(r\phi/\lambda)-C_2K_0(r\phi/\lambda)]. \quad (25)$$

It is interesting at this point to evaluate the flux in the hole for the case $H_0=0$ using (25), (20), and (21):

$$\pi r_1^2H_1=\frac{hc}{e^*}n\bigg/\left(1+\frac{I_0(\beta)K_1(\alpha)+K_0(\beta)I_1(\alpha)}{I_0(\beta)K_0(\alpha)-I_0(\alpha)K_0(\beta)}\frac{2\lambda}{r_1\phi}\right) \quad (26)$$

$$\underset{d\ll r_1}{\longrightarrow}\frac{hc}{e^*}n\bigg/\left(1+\frac{2\lambda^2}{rd\phi^2}\right). \quad (27)$$

If ϕ^2 is set equal to 1, Eq. (27) will be recognized as the expression for the quantized flux for a thin ring given by Bardeen,[7] Kellers and Zumino,[8] and others.[6,14,17] This expression, however, is not exactly the magnetic moment, the quantity measured experimentally. In addition to the error of neglecting the flux in the superconductor, which is a small term of the order of d/r, the order parameter ϕ as it will be shown depends on n (and H_0).

Next, a self-consistent solution for ϕ is obtained directly from (1),

$$\phi^2=1-a^2, \quad (28)$$

where an average over the superconductor has been substituted for the spatially varying terms:

$$a^2=\left(\frac{\lambda e^*}{\kappa\hbar c}\right)^2\left\langle\left(A(r)-\frac{\hbar cn}{e^*r}\right)^2\right\rangle_{\text{av}}, \quad (29)$$

where $\langle\Theta\rangle_{\text{av}}$ represents the spatial average of Θ and is defined as

$$\langle\Theta\rangle_{\text{av}}=\frac{2}{(r_1+d)^2-r_1^2}\int_{r_1}^{r_1+d}r\,\Theta(r)dr.$$

Solutions in the Limit $d\ll\lambda$

In the limit of $d\ll\lambda$, Eqs. (19) and (25) become

$$A(r)=\frac{hc}{e^*\pi r_1^2}\{\tfrac{1}{2}r_1(\mathfrak{h}_0-n)+\tfrac{1}{2}(r-r_1)[\mathfrak{h}_0+(1+\gamma^2\phi^2)n]\}/\times(1+\tfrac{1}{2}\gamma^2\phi^2), \quad (30)$$

$$H(r)=\frac{hc}{e^*\pi r_1^2}\left\{\left(1+\frac{r-r_1}{d}\frac{\gamma^2\phi^2}{2}\right)\mathfrak{h}_0+\tfrac{1}{2}\gamma^2\phi^2\left(1-\frac{r-r_1}{d}\right)n\right\}\bigg/(1+\tfrac{1}{2}\gamma^2\phi^2), \quad (31)$$

where $\mathfrak{h}_0$ is the reduced external field measured in units of the field associated with one flux quantum,

$$\mathfrak{h}_0=(e^*\pi r_1^2/hc)H_0, \quad (32)$$

and γ^2 is a dimensionless ratio,

$$\gamma^2=r_1d/\lambda^2. \quad (33)$$

Equations (30) and (31) are now used to evaluate all the other properties of system. The reduced "gap" becomes

$$\phi^2=1-\left(\frac{\lambda}{\kappa r_1}\right)^2\left[(\mathfrak{h}_0-n)^2+(\mathfrak{h}_0-n)\{\mathfrak{h}_0+(1+\gamma^2\phi^2)n\}\frac{d}{r_1}+\{\mathfrak{h}_0+(1+\gamma^2\phi^2)n\}\frac{d^2}{3r_1^2}+\cdots\right]\bigg/(1+\tfrac{1}{2}\gamma^2\phi^2)^2. \quad (34)$$

It is noted for later reference that the last term on the right is the first term in d/r which does not contain $(\mathfrak{h}_0-n)$ as a factor. If $\mathfrak{h}_0-n\ll1$, $\gamma^2nd/r\ll1$, the order parameter on the right-hand side of (34) can be replaced by 1, and one obtains for ϕ in this limit as a function of $\mathfrak{h}_0$ a set of intersecting "parabolas,"

$$\phi^2=1-\left(\frac{\lambda/\kappa r_1}{1+\frac{1}{2}\gamma^2}\right)^2(\mathfrak{h}_0-n)^2, \quad (35)$$

which are spaced with period 1 as n takes on its integral values. The maxima of these "parabolas" are located on a quadratic envelope given by

$$\phi^2=1-\frac{1}{3}\left(\frac{\lambda d}{\kappa r_1^2}\right)^2\mathfrak{h}_0^2. \quad (36)$$

The evaluation of the Gibbs free energy (7) using (30) and (31) yields

$$\mathfrak{g}=-\phi^4\left\{1-\frac{d}{r_1\kappa}\frac{(\mathfrak{h}_0-n)^2}{1+\gamma^2\phi^2/2}+\cdots\right\}, \quad (37)$$

where the reduced function $\mathfrak{g}$ has been introduced:

$$\mathfrak{g}=\frac{\mathcal{G}_{SH}-\mathcal{G}_{NH}}{(H_{cb}^2/8\pi)2\pi r_1d}. \quad (38)$$

In the same limit for which (35) and (36) are valid the $\mathfrak{g}$ versus $\mathfrak{h}_0$ curves are also a set of intersecting "parabolas,"

$$\mathfrak{g}=-1+[2(\lambda/\kappa r_1)^2(1+\tfrac{1}{2}\gamma^2)^{-1}](\mathfrak{h}_0-n)^2, \quad (39)$$

whose minima lie on a quadratic envelope

$$\mathfrak{g}=-1+\tfrac{2}{3}(1+\tfrac{1}{2}\gamma^2)(\lambda d/\kappa r_1^2)^2\mathfrak{h}_0^2. \quad (40)$$

Neglecting terms of the order d/λ, evaluation of (8) for the magnetic moment gives

$$\mathfrak{M}=\frac{1}{4\pi}\frac{\frac{1}{2}\gamma^2\phi^2}{1+\frac{1}{2}\gamma^2\phi^2}\frac{hc}{e^*}(n-\mathfrak{h}_0). \quad (41)$$

In the region where ϕ^2 can be replaced by 1, this expression is equivalent to that given by others.[6–8,14,17] In a similar manner the average current density is found from (10) to be

$$\frac{4\pi}{c}\bar{J}=\frac{1}{\pi r_1^2 d}\,\frac{\frac{1}{2}\gamma^2\phi^2}{1+\frac{1}{2}\gamma^2\phi^2}\,\frac{hc}{e^*}(n-\mathfrak{h}_0). \tag{42}$$

Equations (41) and (42) show that persistent currents in the absence of a magnetic field differ in nature from the currents associated with the Meissner effect. The Meissner effect represented by the last term gives the usual diamagnetism, whereas the persistent current represented by the first term is quantized and "paramagnetic."

It is seen that, in general, the various properties above depend on n and $\mathfrak{h}_0$ in a complex way. They cannot readily be expressed in terms of n and $\mathfrak{h}_0$ for arbitrary values of the parameters because (34) is at least a cubic equation in ϕ^2.

Critical Conditions

The critical conditions are obtained by examining the properties of the Gibbs free energy, which will be done now. Except when $n\approx\mathfrak{h}_0$ the inequality $|n-\mathfrak{h}_0|\gg(d/r_1)|\mathfrak{h}_0+(1+\gamma^2\phi^2)n|$ will be satisfied if n and $\mathfrak{h}_0$ are not too large. In this case (34) can be approximated by

$$\phi^2=1-(\lambda/\kappa r_1)^2(\mathfrak{h}_0-n)^2/(1+\tfrac{1}{2}\gamma^2\phi^2)^2. \tag{43}$$

Combining this with (37), the free energy can be expressed in terms of ϕ^2 and γ^2 only, which will allow certain statements to be made independent of n or $\mathfrak{h}_0$:

$$\mathfrak{g}=-\phi^4[1-\gamma^2(1-\phi^2)]. \tag{44}$$

Examination of this equation shows that there are two regions of interest corresponding to $\gamma^2\leq1$ and $\gamma^2\geq1$.

Case 1. $\gamma^2\leq 1$. For this case $\mathfrak{g}=0$ has only the root $\phi=0$. Assuming n to be fixed, the critical condition is obtained by setting $\phi=0$ in (43)

$$|\mathfrak{h}_0-n|_c=\kappa r_1/\lambda. \tag{45}$$

Case 2. $\gamma^2\geq 1$. In addition to the above root of the $\mathfrak{g}=0$ equation, there is another given by

$$\phi_c^2=1-1/\gamma^2, \tag{46}$$

from which with (43) the following critical condition is obtained

$$|\mathfrak{h}_0-n|_c=[(1+\gamma^2)/2\gamma](\kappa r_1/\lambda) \tag{47}$$

$$\xrightarrow[\gamma^2\gg1]{}\tfrac{1}{2}\gamma(\kappa r_1/\lambda). \tag{48}$$

It is clear that this latter root corresponds to the equilibrium thermodynamic phase transition because, under an external agent, ϕ^2 starting from 1 will reach $\phi_c^2=1-1/\gamma^2$ before it will reach $\phi_c^2=0$.

Also for this case $\mathfrak{g}$ is positive between the two roots and has a maximum of

$$\mathfrak{g}_{\max}=\phi_m^6(2-3\phi_m^2)^{-1} \tag{49}$$

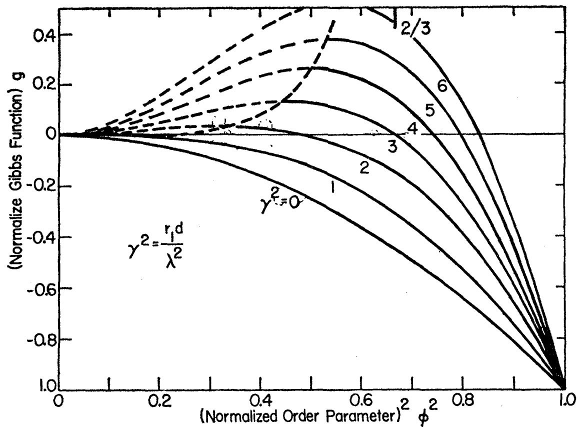

FIG. 2. Reduced Gibbs free energy versus reduced order parameter for various γ^2.

occurring at

$$\phi_m^2=\tfrac{2}{3}(1-1/\gamma^2). \tag{50}$$

The value of $|\mathfrak{h}_0-n|$ at this point is

$$|\mathfrak{h}_0-n|=[\tfrac{1}{3}(2+\gamma^2)]^{3/2}(1/\gamma)(\kappa r_1/\lambda) \tag{51}$$

$$\xrightarrow[\gamma^2\gg1]{}(\tfrac{1}{3})^{3/2}\gamma^2(\kappa r_1/\lambda). \tag{52}$$

The region between $\mathfrak{g}_{\max}$ and the second root defines a thermodynamically metastable region and (51) gives the critical conditions at the extreme metastable limit.

Equation (44) for $\mathfrak{g}$ has been plotted in Fig. 2 for various values of γ^2. It is seen that for $\gamma^2\leq1$, $\mathfrak{g}$ and ϕ approach 0 together, defining a second-order phase transition; whereas for $\gamma^2\geq1$, $\mathfrak{g}$ becomes 0 at a finite value of ϕ, defining a first-order phase transition. Figure 3 shows on a $\phi^2-\gamma^2$ plot this same information, where the thermodynamic regions of stability, metastability, and instability are quite evident. These curves are very similar to, and have the same qualitative features as,

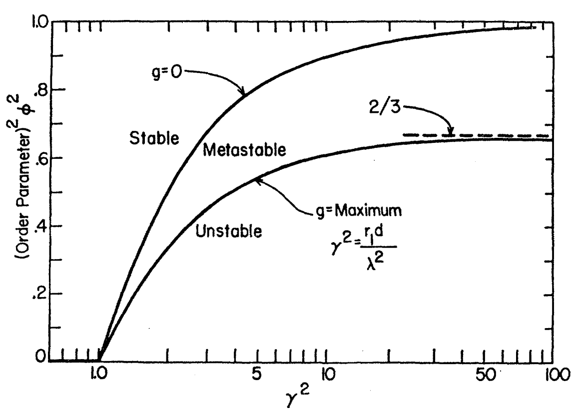

FIG. 3. Critical ϕ^2 versus γ^2.

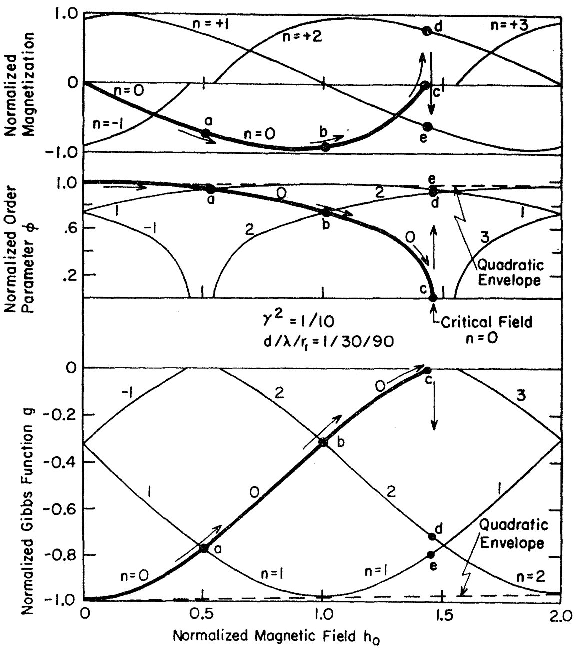

FIG. 4. Magnetization, order parameter, and Gibbs free energy versus magnetic field for $\gamma^2=\frac{1}{10}$.

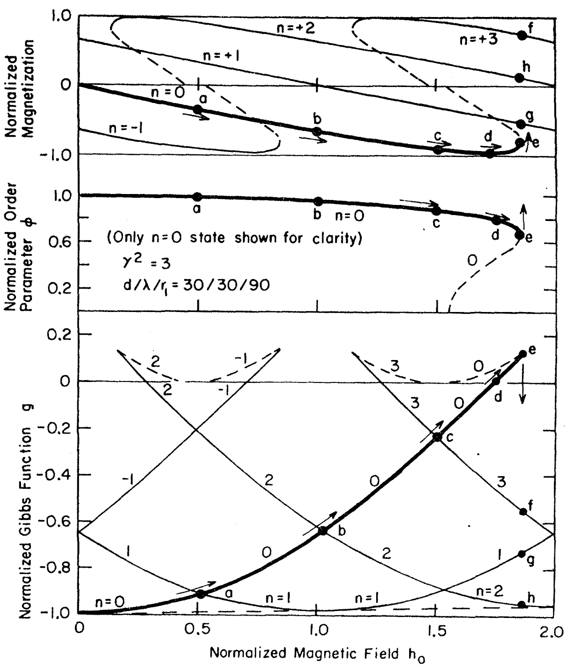

FIG. 5. Magnetization, order parameter, and Gibbs free energy versus magnetic field for $\gamma^2=3$.

the solutions of the singly connected film[28–30] with the ratio d/λ corresponding to γ^2. Plots of the magnetization, order parameter, and free energy versus $\mathfrak{h}_0$ for various n illustrating the two cases $\gamma^2<1$ and $\gamma^2>1$ are shown in Figs. 4 and 5, respectively. Discussion of how to relate these curves to physical processes is deferred until the next section.

Periodicity of the Transition Temperature

Very near the transition temperature $\gamma^2<1$ so that the phase transition is second order, which means that $\mathfrak{g}$ and ϕ approach zero together. For this particular calculation, no assumption is necessary concerning the magnitude of n and $\mathfrak{h}_0$. The critical temperature is determined implicitly by setting $\phi=0$ in Eq. (34),

$$\left(\frac{\kappa r_1}{\lambda}\right)^2=(\mathfrak{h}_0-n)^2+(\mathfrak{h}_0^2-n^2)\frac{d}{r_1}+(\mathfrak{h}_0+n)^2\frac{d^2}{3r_1^2}+\cdots, \quad (53)$$

where the temperature dependence is contained in κ and λ. Using the usual temperature dependences $\kappa(t)=\kappa(0)(1+t^2)^{-1}$ and $\lambda^2(t)=\lambda^2(0)(1-t^4)^{-1}$, where $t=T/T_c$, one obtains

$$\left(\frac{1-t^2}{1+t^2}\right)\left(\frac{\kappa(0)r_1}{\lambda(0)}\right)^2=(\mathfrak{h}_0-n)^2+(\mathfrak{h}_0^2-n^2)\frac{d}{r_1}+(\mathfrak{h}_0+n)^2\frac{d^2}{3r_1^2}+\cdots. \quad (54)$$

This equation represents a set of intersecting "parabolas" in the $\mathfrak{h}_0-t$ plane whose vertices lie on a "quadratic" envelope. In this case because the system is at the phase boundary between the superconducting and normal state, it is correct to assume that the quantum number *can* change at points of intersections of various curves. The value of the field $\mathfrak{h}_m$ for which the temperature is a local maximum is found by solving $dt/d\mathfrak{h}_0=0$ for $\mathfrak{h}_0$.

$$\mathfrak{h}_m=\left(1-\frac{d}{r_1}+\frac{1}{3}\frac{d^2}{r_1^2}+\cdots\right)n. \quad (55)$$

Using (55), Eq. (53) can be put into the following form:

$$\left(\frac{\kappa r_1}{\lambda}\right)^2=\frac{1-t^2}{1+t^2}\left(\frac{\kappa(0)r_1}{\lambda(0)}\right)^2=(\mathfrak{h}_0-\mathfrak{h}_m)^2\left(1+\frac{d}{r_1}\right)+\frac{(\mathfrak{h}_0-\mathfrak{h}_m)^2+\mathfrak{h}_m^2}{3}\left(\frac{d}{r_1}\right)^2+\cdots. \quad (56)$$

The first term on the right-hand side of (56) gives the periodic term for the transition temperature,

$$\left(\frac{\kappa r_1}{\lambda}\right)^2=\frac{1-t^2}{1+t^2}\left(\frac{\kappa(0)r_1}{\lambda(0)}\right)^2=\left(1+\frac{d}{r_1}\right)(\mathfrak{h}_0-\mathfrak{h}_m)^2, \quad (57)$$

and the envelope curve going through the maxima is obtained by setting $\mathfrak{h}_0=\mathfrak{h}_m$:

$$\left(\frac{\kappa r_1}{\lambda}\right)^2=\frac{1-t^2}{1+t^2}\left(\frac{\kappa(0)r_1}{\lambda(0)}\right)^2=\tfrac{1}{3}\mathfrak{h}_m^2\left(\frac{d}{r_1}\right)^2. \quad (58)$$

[28] V. L. Ginzburg, Doklady Akad. Nauk SSSR **83**, 385 (1952).
[29] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **34**, 113 (1958) [translation: Soviet Phys.—JETP **7**, 78 (1958)].
[30] D. H. Douglass, Jr., Phys. Rev. Letters **6**, 346 (1961).

Equations (57) and (58) are identical to similar expressions given by Tinkham[18] when κ from (6) is put into them and describe adequately the measurements of Little and Parks[31] on the variation of the transition temperature with field. Putting κ into (58) and rearranging, one obtains for the envelope curve

$$H_m^2=24\left(\frac{\lambda}{d}\right)^2 H_{cb}^2, \tag{59}$$

which will be recognized immediately as the critical field curve given by the GL theory for a singly connected film.[28]

B. The Composite Hollow Cylinder

Consider a composite superconducting hollow cylinder consisting of superconductor a over an angular region θ_o and superconductor b over angular region $2\pi-\theta_o$. Analysis of this problem proceeds in a straightforward way. First, one can find good quantum numbers n. This comes solely from the fact that the sample is multiply connected plus the condition of single-valuedness, $\Psi(\theta)=\Psi(\theta+2\pi)$, of the order parameter.[32] The only influence that variations in the parameters of the superconductor or deviations of the cross section from circular symmetry have is to distort the various curves in the $\mathfrak{g}-\mathfrak{h}_0$ plane while keeping the "topology" intact; a different way of saying this is the circular hollow cylinder can be changed or deformed adiabatically to any particular doubly connected configuration keeping the quantum number constant. For weak fields and for $r\gg\xi_0$, $r\gg\lambda$, and $d\ll\lambda$, one obtains expressions which are quite similar to those of the previous section. The magnetization is the same

$$\mathfrak{M}=\frac{1}{4\pi}\frac{\gamma^2/2}{1+\gamma^2/2}\frac{hc}{e^*}(n-\mathfrak{h}_0), \tag{60}$$

where $\gamma^2=(rd)/\lambda^2$. Here λ is a weighted average between λ_a and λ_b,

$$\lambda=\left[\frac{\theta_o\lambda_a^2+(2\pi-\theta_o)\lambda_b^2}{2\pi}\right]^{1/2}. \tag{61}$$

Thus, it is seen that if $\gamma^2\gg1$, which is the usual case, the magnetization and fluxoid quantization is unchanged by making the cylinder composite. In a similar way the order parameters in superconducting sections a and b are

$$\phi_a^2=1-\left\{\frac{(\lambda_a/\kappa_a r_1)^2(\lambda_a/\lambda)^4(n-\mathfrak{h}_0)^2}{(1+\frac{1}{2}\gamma^2)^2}\right\}, \tag{62}$$

$$\phi_b^2=1-\left\{\frac{(\lambda_b/\kappa_b r_1)^2(\lambda_b/\lambda)^4(n-\mathfrak{h}_0)^2}{1+\frac{1}{2}\gamma^2}\right\}, \tag{63}$$

and the free energy is

$$\frac{\mathfrak{G}_{SH}-\mathfrak{G}_{NH}}{2\pi r_1 d}=\frac{\theta_o}{2\pi}\frac{H_a^2}{8\pi}(-2\phi_a^2+\phi_a^4)+\frac{2\pi-\theta_o}{2\pi}\frac{H_b^2}{8\pi}(-2\phi_b^2+\phi_b^4)+\frac{r_1}{16\pi d}\frac{\frac{1}{2}\gamma^2}{1+\frac{1}{2}\gamma^2}\left(H_0-\frac{2\hbar cn}{e^*r_1^2}\right)^2, \tag{64}$$

where H_a and H_b are the bulk critical fields for superconductors a and b, respectively.

III. DISCUSSION

The results derived in the previous section made use of the assumption that the fluxoid quantum number n remains constant as the external field is changed, as long as the sample is in the superconducting state. This assumption is consistent with London's idea of "stiff wave functions" or that the "canonical momentum" should remain invariant under a change in the magnetic field; the evaluation of the "canonical momentum" shows that it is proportional to n.

From a microscopic point of view,[10,33] in the absence of a magnetic field the state characterized by the fluxoid quantum number n corresponds to every "Cooper pair" having n units of angular momentum; a state of different n corresponds to a complete repairing of all the electrons so that each of the new pairs have the angular momentum corresponding to the new n. This means that any flucutation or perturbation capable of changing n would have to supply or take from each pair the same number of units of angular momentum simultaneously.[34] The fact that states of different n differ by macroscopic amounts of angular momentum means that matrix elements connecting different states are vanishingly small. In addition to implying nearly infinite lifetimes for metastable states, this result says that the degeneracy at certain points will not be removed and the $\mathfrak{g}$ versus $\mathfrak{h}_0$ curves will not break up into bands. Thus, the only likely perturbation capable of changing n is one for which the pairs make mechanical contact with the lattice (i.e., to go into

[31] W. A. Little and R. D. Parks, Phys. Rev. Letters 9, 9 (1962).

[32] The main difference between the present case and the homogeneous hollow cylinder is that the phase η of Eq. (11) instead of satisfying Eq. (14), (16), is given by a more complicated function $\eta(\theta)$ such that $\eta(\theta+2\pi)=\eta(\theta)+2\pi n$. In the limit $r\gg\xi$, η can be approximated by a series of linear segments with two different slopes in the regions of superconductors a and b

[33] Gregor Wentzel, Proc. Natl. Acad. Sci. U. S. (to be published).

[34] All of the pairs changing simultaneously is not essential as is sometimes assumed. A more probable process is for a fluctuation or a perturbation to nucleate a new state over a coherence length at a "weak" spot; if energetically favorable the new state will grow.

the normal state) which must be energetically favorable. The most convincing evidence that n is constant under change of the magnetic field is that the experiments[3,4] have shown that the metastable persistent current states can be reached by turning off a magnetic field; if n were not constant and were allowed to change during this process then it would be quite likely that the system would always end up in the $n=0$ states of no current.

In regard to the other assumption that the system remains superconducting to the extreme thermodynamic metastable limit, there are no theoretical reasons at present[35] for this. However, from the discussion of the previous paragraph it is hard to see how the matrix elements or transition probabilities could be effected by having the initial state in the thermodynamic metastable region; the arguments concerning re-pairing and exchange of macroscopic amounts of angular momentum should be the same. Using these assumptions it is now possible to interpret the $\mathfrak{g}$ versus $\mathfrak{h}_0$ curves in Figs. 4 and 5.

For the $\gamma^2<1$ case (chosen as $\frac{1}{10}$ for an illustrative example) consider a specimen which is initially in the $n=0$ state; in Fig. 4 the system is in the state characterized by the intersection of the $n=0$ curve with the $\mathfrak{g}$ axis. As the magnetic field is increased the system will follow along the $n=0$ curve. When point a is reached the $n=0$ state is degenerate with the $n=1$ state; with the previous assumption, the system remains in the $n=0$ state and passes successively through points a and b until point c is reached. At this point, because $\mathfrak{g}=\phi=0$, the system will go momentarily into the normal state. Depending on the rate of change of the system at c and on various fluctuations, either 1 or 2 flux quanta will leak into the hole of the sample allowing the system to become superconducting again with the final state being either at d or e. There is no way of knowing from thermodynamics alone what the final state will be; full knowledge of the kinetics must be in hand. Upon further increase of the external field, the system will move along the new curve of constant n until again $\mathfrak{g}=0$ and more flux quanta leak into the hole; this process will repeat again and again until the point is reached where the envelope curve intersects the $\mathfrak{g}=0$ line.

It is now evident what a state of persistent current is and how to generate it. The persistent current states are represented by the intersection of the various curves with the negative $\mathfrak{g}$ axis; in this case there are only three such states corresponding to $n=0, \pm 1$. These states may be produced by removing a magnetic field from the specimen; as the field is reduced the system will "ride" the curves of constant n in the opposite direction and flux quanta will leak out at the extremities where $\mathfrak{g}=0$. Depending on which state the system has fallen into as $\mathfrak{h}_0 \rightarrow 0$, the system will end up in a particular current carrying state (which includes the 0 current state). If it is desired to put the system into the $n=1$ current carrying state, for example, one could achieve this by turning on a field $\mathfrak{h}_0$ to any value between 0.5 and 1.5 while the specimen is in the normal state. Then the temperature is lowered below the transition temperature T_c of the sample. As the sample first becomes superconducting near T_c the curves in the $\mathfrak{g}-\mathfrak{h}_0$ plane are "truncated parabolas" situated at $\mathfrak{h}_0$ equal to an integer (i.e., system is superconducting near $\mathfrak{h}_0=$integer and normal near $\mathfrak{h}_0=$half-integer). As the temperature is lowered the superconducting "region" near each integer increases toward the half-integers; at some temperature one would expect that the sample would drop into the $n=1$ state and remain there upon further lowering of the temperature.[36] Upon removal of the field the system will be in the $n=1$ current carrying state. It is clear that the critical persistent current corresponds to the highest state on the negative $\mathfrak{g}$ axis.

For the $\gamma^2\geq 1$ case shown in Fig. 5 (γ^2 has been chosen equal to 3 for an illustrative example) most of the previous discussion for the $\gamma^2\leq 1$ case carries over. One difference has to do with thermodynamic metastability region. Starting with $n=\mathfrak{h}_0=0$ and assuming n to be constant, the system will move as a function of $\mathfrak{h}_0$ along the $n=0$ curve until a point is reached at which point $\mathfrak{g}=0$; the sample may go into the normal state but the arguments presented earlier lead one to believe that the system remains superconducting. It is assumed here that the system does remain superconducting until the extreme metastable limit (point e on the $n=0$ curve); at this point one, two, or three flux quanta, depending on conditions, will leak in, and the process repeats again and again as the field is increased as before. If the system remains superconducting to the metastable limit, the critical conditions will be given by (51) and not (47). Also the critical persistent current as generated by removal of a magnetic field will correspond to the highest state on the $\mathfrak{g}$ axis which will occur for *positive* $\mathfrak{g}$. The *critical* persistent current density is obtained directly by putting (50) and (51) into (42):

$$\frac{4\pi}{c}\bar{J}_{\text{crit}}=\frac{1}{d}\left(\frac{hc}{e^*\pi r_1^2}\right)\left(\frac{\kappa r_1}{\lambda}\right)(\gamma^2-1)\left[\frac{1}{27}\left(1+\frac{2}{\gamma^2}\right)\right]^{1/2}, \quad (65)$$

which is good when $\gamma^2\geq 1$; when $\gamma^2\leq 1$, $J_{\text{crit}}=0$. The state corresponding to the *maximum* persistent current is computed by finding the n such that $dJ/dn=0$; this calculation yields $\phi^2=\frac{2}{3}$ corresponding to that n.

[35] Bloch and Rorschach (see Ref. 17) have found for the charged Bose-Einstein gas similar regions of metastability. Their calculations show that the lifetime is essentially infinite.

[36] In the experiment reported by Deaver and Fairbank (see Ref. 3), one case out of about 50 is reported for which the system ended in the $n=0$ state instead of the $n=1$ state after lowering the temperature.

Using this along with (43) and (42) yields

$$\frac{4\pi}{c}\bar{J}_{\max}=\frac{1}{d}\left(\frac{hc}{e^*\pi r_1^2}\right)\left(\frac{\kappa r_1}{\lambda}\right)\frac{\gamma^2}{\sqrt{27}}, \qquad (66)$$

which is good for all γ^2. The ratio is found to be

$$\bar{J}_{\mathrm{crit}}/\bar{J}_{\max}=(1-3/\gamma^4+2/\gamma^6)^{1/2}, \qquad (67)$$

showing that $J_{\max}>J_{\mathrm{crit}}$. In addition to describing the persistent current state $\mathfrak{h}_0=0$, (65), (66), and (67) are valid for the current state in a magnetic field as well. Recently, Mecereau and Hunt[37] have measured critical persistent currents in hollow thin samples by a rather interesting technique. In these experiments $\gamma^2\gg1$, which makes the comparison of their results with the current implied by Eq. (48) for the thermodynamic phase transition and Eq. (52) or (65) for the extreme metastable limit quite unambiguous. First, the temperature dependences are different; near $t\sim1$, the thermodynamic transition yields $J\propto\Delta t$ whereas the extreme metastable transition implies $J\propto(\Delta t)^{3/2}$. The measurements show clearly that $J\propto(\Delta t)^{3/2}$ corresponding to the latter case. Secondly, the experimental measurements with a not unreasonable $\lambda(0)$ agree in magnitude with the current at the metastable transition which is larger than the current corresponding to the thermodynamic transition by a factor of γ.

It should be pointed out that the calculations in the preceding section yield the result that the various properties of the hollow cylinders are strictly periodic in the field with a period corresponding to unit quantum; the nonlinear "mixing" terms in the theory fail to generate any "harmonics." This is of interest in view of the fact that Little and Parks[38] have observed "harmonic" structure on certain samples under special conditions in their measurements of the periodicity of the transition temperature with magnetic field. They found periods which they suggested could "be indicative of the existence of multiple pairs" corresponding to e^* equal to $4e$ and $8e$.[39]

In summary, the properties of a thin, hollow superconducting cylinder have been considered without making the approximation that the energy gap (order parameter) does not change with magnetic field or fluxoid quantum number.

When $rd/\lambda^2\leq1$, and for a fixed n, the energy gap goes smoothly to zero with magnetic field, a second-order phase transition, with the magnetic moment, the current, and the free energy being affected accordingly. Also for this limit the transition temperature is periodic with field as shown experimentally by Little and Parks[31] and agrees with the calculation of Tinkham.[18]

In the limit $rd\geq\lambda^2$, and for a fixed n, the energy gap drops discontinuously to zero at the critical point, a first-order phase transition, again with influence on the other properties of the superconductor.

In either case arguments are given for assuming that n is constant under a change of magnetic field as long as the system remains superconducting. This leads to metastable states which for the $rd\geq\lambda^2$ case includes states which are thermodynamically metastable as well. The experiments on flux quantization[3,4] and critical persistent currents[37] can be explained by making such an assumption.

IV. ACKNOWLEDGMENTS

The author wishes to acknowledge many fruitful discussions with M. H. Cohen and L. M. Falicov. In addition, L. M. Falicov collaborated on the solution of the composite cylinder.

This work was partially supported by the Army Research Office and the National Aeronautics and Space Administration. The author would also like to acknowledge the support of the general research facilities of the Institute for the Study of Metals provided by the National Science Foundation, the Atomic Energy Commission, and the Advanced Research Projects Agency.

[37] J. E. Mecereau and T. K. Hunt, Phys. Rev. Letters **8**, 243 (1962).

[38] W. A. Little and R. D. Parks, in Proceedings of the Eighth International Conference on Low Temperature Physics (to be published).

[39] An alternative and plausible but less exciting explanation is possible. Using the results of the previous section for the critical field for a fixed n and plausible assumptions concerning the nature of the particular sample, the appearance, the shape, and the sequence of periods versus current of these "harmonics" can be accounted for. This possible explanation has to do with the fact that this structure is only observed when operating on the low-temperature end of the resistance "tail." Under these conditions only a small portion of the sample has a transition temperature this low; most of the sample has a higher transition temperature. The observed voltage is a superposition of the effect of the magnetic field on these two different regions. The magnetic field produces a voltage with the expected periodicity on that portion of the sample having a transition temperature equal to the operating temperature. For the portion of the sample having a transition temperature greater than the operating temperature the system follows on a $\mathfrak{g}-\mathfrak{h}_0$ plot the curves of constant n going through the "saw-tooth" sequence producing a voltage of the same shape: "right-handed teeth" for increasing field and "left-handed teeth" for decreasing field. If $\gamma^2<1$, which was the case, then the change in flux at the edge of the "teeth" would correspond to only one quanta; from this it is easy to see that the voltage would have unit period but with a variable phase determined by the intercept of the $n=0$ curve with the $\mathfrak{g}=0$ axis. This intercept can be varied continuously, either by changing the temperature or the monitoring current; for particular values of the phase the superposition of these various voltages can give the observed "harmonics."