Thermoelectric effect in superconductors

R. M. Arutyunyan and G. F. Zharkov

P. N. Lebedev Physics Institute, Academy of Sciences of the USSR

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The problem of the thermoelectric effect in a superconducting ring is considered within the framework of the macroscopic Ginzburg-Landau theory. An exact solution is obtained for the model case of a homogeneous superconducting cylinder with a prescribed normal-excitation current I_n . It is shown that the total circumfluent current I and the magnetic field H_1 in the cavity of the cylinder arise as the response to the prescribed external current I_n . A profound analogy is found to exist between the behavior of the thermoelectric system and the behavior of a hollow superconducting cylinder in an external field. Both systems are characterized by the presence of quantum levels, which specify the possible number m of flux quanta frozen in the cavity. It is shown that even in the absence of an external field it becomes possible, as the temperature is raised, for a thermoelectric ring in the m = 0 state to go over spontaneously into states with m > 0. The "giant" thermoelectric effect observed in a number of experiments is interpreted as being due to transitions of the system to higher levels, i.e., to $m \rightarrow m + 1$ transitions. It is shown that a thermoelectric ring should go over into the normal state not at the critical temperature T_c , but at some $T_c^* < T_c$. The possible hysteresis effects and the role of impurities, fluctuations, and inhomogeneities in a thermoelectric system are discussed. A number of predictions are made which can be verified in experiment.

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§I. INTRODUCTION

The problem of the thermoelectric effect in superconductors has recently been discussed intensively in the literature. Here we shall mention only a few points, referring the reader to Ref. 1 for details and the history of the problem. The effect in question consists in the fact that a current arises in a superconducting ring made up of two dissimilar metals when the soldered joints are maintained at different temperatures T_1 and T_2 . Outwardly, this effect is entirely similar to the ordinary thermoelectric effect that occurs in a normal circuit, with the only important difference that the thermoelectric power is equal to zero in a superconducting ring in the steady state.^{1) 1} In view of this, the nature of the current generated in the superconducting circuit is somewhat of a puzzle, and different viewpoints have been expressed apropos of this in the literature. According to ideas first put forward in Refs. 2 and 3, and subsequently repeated often in the literature,⁴⁻⁹ the thermoelectric current in a superconducting ring has a purely quantum character, since it is connected with the phase difference of the wave function in the superconductor. Such a phase difference is, by assumption, produced when the ring is heated, which leads to the appearance of a superconducting current proportional to the phase gradient: $\mathbf{j} \propto \nabla \varphi$. An entirely different viewpoint is expressed in Ref. 1 (see also Ref. 10), where the appearance of the thermoelectric current is related to the acceleration of the superconducting condensate by the nonstationary electric field that arises in the superconductor as it is heated, i.e., the classical character of the appearance of the thermoelectric current is emphasized. According to the latter point of view,^{1,10} the thermoelectric current has essentially the same character as the ordinary Meissner currents that arise in a

superconductor located in an external magnetic field. In the present paper we shall adhere to this later point of view. Let us note in this connection that the difference between these two approaches is not purely terminological, since the interpretation of the thermoelectric current as being due solely to the appearance of a phase difference in the superconductor leads sometimes to plain errors (see the critical comments made in Ref. 10 in connection with Pickett's incorrect paper⁹).

Thermoelectric currents have been observed in heterogeneous superconducting rings in a number of experimental investigations.⁵⁻⁸ But if in the first measurements, performed by Zavaritskii,⁵ there were observed thermoelectric fluxes at the level of $10^{-2} \Phi_0$, where $\Phi_0 = 2 \times 10^{-7} \,\text{G-cm}^2$ is the flux quantum (which, on the whole, was in accord with the magnitude of the effect expected on the basis of the theoretical estimates [for greater details, see Ref. 1)], much larger fluxes were often observed in the subsequent measurements⁶⁻⁸ (see, in particular, Ref. 8, which reports the observation of fluxes at the level of $10^2 \Phi_0 - 10^3 \Phi_0$, i.e., at a level several orders of magnitude higher than the theoretical estimates). The nature and temperature dependence of this "giant" thermoelectric effect in superconductors still remain unelucidated. Thus, it is postulated in Ref. 6 that the parasitic effects connected with the uncontrolled external magnetic flux trapped in the circuit can play a role; in Ref. 9 an attempt is made to relate the observed giant thermoelectric flux to strong currents generated on the outer surface of the superconducting ring [the presence of such currents is argued in Ref. 9 by the necessity to satisfy certain phase relations (see also Ref. 10)]; in Ref. 11 a kinetic theory is propounded according to which strong secondary currents are

generated on the inner surface of the ring²⁾ as a result of the presence of nonequilibrium effects; and in Refs. 1 and 10 the possible role of the inhomogeneity at the soldered joints is discussed. The lack of a clear understanding of the experimentally observed effects is due, in particular, to difficulty of a consistent theoretical investigation of an inhomogenous superconducting system that is in a nonequilibrium state (i.e., in the presence of a temperature gradient) and with allowance for the significantly different geometric factors that characterize specific experiments.^{5–8}

In the present paper we consider the thermoelectric effect in a superconducting ring within the framework of a simplified model that allows us to obtain an exact solution to the problem in the entire temperature range extending right up to $T = T_c$. The formulation of the problem is as follows. Let us first consider a homogeneous normal ring at a temperature T (the role of the inhomogeneity is considered later). We specify the total current I_n circulating inside the ring; a magnetic flux Φ_n is then prescribed in the normal ring. The question arises: What total current I and magnetic flux Φ will be established in the ring if it goes over into the superconducting state at $T < T_c$ under the conditions of the prescribed normal-excitation current I_n .

Actually, we limit ourselves below to a sample having the form of an infinite—along the z axis—hollow cylinder with inside radius r_1 and outside radius r_2 . In the case of a cylindrical normal sample, it is easy to find that the total circulating current I_n is connected with the field H_{1n} inside the cavity by the relation $I_n = cH_{1n}/4\pi$, the normal-current density j_n being distributed along the radius of the cylinder according to the law.

$$j_n(r) = \frac{Q}{r}, \quad I_n = \int_{r_1} j_n(r) dr = Q \ln \frac{r_2}{r_1}, \quad Q = \frac{c}{4\pi} \frac{H_{1n}}{\ln(r_2/r_1)}.$$
(1.1)

Under ordinary conditions the normal thermoelectric current I_n is proportional to the temperature difference $T_2 - T_1$ between the soldered joints, and arises only in an inhomogeneous sample: $I_n = (b_a - b_b)(T_2 - T_1)$, where b_a and b_b are the thermoelectric coefficients of the metals a and b. In our model the normal current is assumed to be uniform (i.e., to be independent of the azimuthal coordinate): $I_n = b (T_2 - T_1)$, where b = const.

We shall, in considering the superconducting cylinder, assume that the sample is homogeneous and is at a definite temperature T. This allows us to ignore the nonequilibrium effects due to the presence of a temperature gradient under real conditions. Actually, we assume that in the present case the nonequilibrium effects play a minor role, and can be neglected. In fact, the temperature gradients are usually small $(\nabla T \sim 10^{-2} \text{ K/cm})$, and it is difficult to expect the strong effect observed in experiment to be due to such a small deviation from equilibrium (see, however, Ref. 11). Some justification for disregarding the disequilibrium state is also that we shall be interested in those aspects of the behavior of the superconducting system which do not depend on the specific mechanisms underlying the onset of the normal-excitation current j_n in the superconductor. Below we shall assume that the current j_n [or, equivalently, the quantity H_{1n} in (1.1)] is a specified external parameter. In order to approximate real conditions, let us set

$$H_{in} = H_{in}^{(0)} \frac{T - T_i}{T_c - T_i}, \qquad (1.2)$$

Here T_1 is some characteristic temperature (T_1 plays the role of the temperature of the cold joint under real experimental conditions); T_c is the critical temperature of the superconductor (if under real conditions $T_{ca} < T_{cb}$, where T_{ca} and T_{cb} are the critical temperatures of the superconductors aand b respectively, then in the model under consideration $T_c = T_{ca}$; the temperature T corresponds to the temperature of the hot joint (under real conditions $T \approx T_{ca}$). At $T = T_1$ (which corresponds to the absence of a temperature gradient) we have $H_{1n} = 0$; at $T = T_c$ we have $H_{1n} = H_{1n}^{(0)}$, where $H_{1n}^{(0)}$ is the maximum field strength attainable in the ring in the normal state. Typical values are $H_{1n}^{(0)} \sim 1$ G and $T_c - T_1 \sim 10^{-2}$ K.

Below we shall have to take into account the temperature dependences of the London depth $\delta_L(T)$ and the coherence length $\xi(T)$ of the superconductor^{12,13}:

$$\xi(T) = \frac{0.74\xi_0}{(1 - T/T_c)^{\frac{1}{2}}}, \quad \delta_L(T) = \varkappa \xi(T); \quad (1.3)$$

here \varkappa is the parameter of the Ginzburg-Landau theory and ξ_0 is the correlation length at T = 0. The expressions (1.3) correspond to the case of pure superconductors. In the case of dirty superconductors we have^{12,13}

$$\xi(T) = \frac{0.85 \left(\xi_0 l\right)^{\gamma_a}}{\left(1 - T/T_c\right)^{\gamma_a}}, \quad \varkappa_d = 0.755 \frac{\xi_0}{l} \varkappa_p, \quad (1.4)$$

where *l* is the mean path; $x_d \gg x_p$ for materials with $l \ll \xi_0$.

The penetration $\delta_L(T)$ depth an important role in the electrodynamics of superconductors: it determines the screening of the field. Allowance for the temperature dependences (1.3) or (1.4) allows us to describe the passage $T \rightarrow T_c$, $\delta_L \rightarrow \infty$ to the normal limit, at which the metal becomes transparent to the field. Under real conditions only a small part of one of the superconductors near the hot joint, and not the entire superconducting ring, becomes transparent at $T \rightarrow T_c$. We shall first study the homogeneous case, which allows us to understand better some important characteristics of the behavior of the system in question; the role of the inhomogeneity will be taken into account in § 6.

So, let us state once more the main points of the model problem.

1) We consider a homogeneous superconducting cylinder at a temperature T close to T_c .

2) We assume that the normal current (1.1) in the superconducting cylinder is prescribed to depend on the temperature according to (1.2), and to be independent of the angle coordinate.

3) We assume that the depth of penetration of the field into the superconductor depends on the temperature according to (1.3) or (1.4).

4) We seek the total current I (or the magnetic flux Φ) in

the superconducting cylinder as the response to a specified external normal current I_n .

We shall solve the formulated problem within the framework of the macroscopic Ginzburg-Landau theory of superconductivity.¹⁴ In §2 we obtain the functional describing the behavior of the superconducting cylinder under conditions of a prescribed normal current. In §3 we solve the electrodynamic problem of determining the total current I for a prescribed normal current I_n . Section 4 is devoted to the self-consistent determination of the order parameter ψ of the superconductor and the determination of the magnetic flux in the cavity of the cylinder as functions of the temperature in the entire temperature range. We also consider in this section a number of hysteresis effects that occur in the ring, and briefly discuss the possible role of the fluctuations. In §5 we consider the transition of a thermoelectric ring from the normal into the superconducting state. In §6 we take the inhomogeneity of a real thermoelectric circuit into account. In the Conclusion we discuss briefly the results obtained in the paper and their connection with experiment.

§2. THE THERMODYNAMIC POTENTIAL OF THE SYSTEM

To solve the formulated problem within the framework of the Ginzburg-Landau theory, we must derive an expression for the thermodynamic potential of the system under the condition that a normal excitation current \mathbf{j}_n is prescribed in the superconductor. Let us, proceeding similarly to the case of a superconductor in a prescribed external magnetic field, ^{15,16} write down the change in the energy of the superconductor:

$$\Delta \mathscr{E} = \Delta Q + \frac{c\Delta t}{4\pi} \int_{\sigma_1} \left[\mathbf{E} \times \mathbf{H} \right] d\sigma_1 - \Delta t \int_{v_*} \mathbf{E} \mathbf{j}_n dv.$$
(2.1)

Here ΔQ is the heat rise in the sample; the second term is the flux of the Poynting vector through the inner surface of the sample ($H_e = 0$ at the outer surface); and the last term is the work done on the prescribed current \mathbf{j}_n by the electromagnetic forces. Evaluating the surface integral, we find that it is equal to

$$\frac{c\Delta t}{4\pi} H_{i} \oint_{\sigma_{i}} Edldz = \mathbf{H}_{i}\Delta t \int_{v_{i}} \operatorname{rot} \mathbf{E} dv = -\frac{\mathbf{H}_{i}}{4\pi} \Delta t \int_{v_{i}} \frac{\partial \mathbf{H}_{i}}{\partial t} dv$$
$$= -V_{i}\Delta \frac{H_{i}^{2}}{8\pi}.$$

Here H_1 is the field inside the cavity, V_1 is the volume of the cavity, V_s is the volume of the superconductor, and $V = V_1 + V_s$ is the total volume occupied by the cylinder. Setting $\mathbf{E} = -c^{-1}\partial \mathbf{A}/\partial t$ in the last term in (2.1) (we assume that no charge is produced in the system, and that the Coulomb potential is equal to zero), and using the inequality $\Delta Q \leq T\Delta S$ (T = const is the temperature, and S is the entropy, of the sample), we reduce (2.1) to the form

$$\Delta\left(F_{s}+\frac{H_{i}^{2}}{8\pi}V_{i}-\frac{1}{c}\int_{V_{s}}\mathbf{A}\mathbf{j}_{n}dv\right)\leq0,$$

where $F_s = \mathscr{C} - TS$ is the free energy of the superconductor. Thus, the functional whose minimum corresponds to the equilibrium state of the system when $T = \text{const}, j_n = \text{const},$ and $H_e = 0$ is

$$\begin{split} \Phi_{s} &= F_{n0} \\ &+ \int_{V_{s}} dv \left\{ -\alpha \left| \Psi \right|^{2} + \frac{\beta}{2} \left| \Psi \right|^{4} + \frac{B^{2}}{8\pi} + \frac{1}{2m^{*}} \left| i\hbar \nabla \Psi \right|^{2} \right. \\ &+ \frac{e^{*}}{c} \mathbf{A} \Psi \left|^{2} \right\} + \frac{H_{1}^{2}}{8\pi} V_{1} - \frac{1}{c} \int_{V_{s}} \mathbf{A} \mathbf{j}_{n} dv. \end{split}$$

$$(2.2)$$

Here we have used the usual—in the Ginzburg-Landau theory¹²⁻¹⁴—expression for the free energy F_s of the superconductor, F_{n0} is the free energy of the normal metal in the absence of a field, $\mathbf{B} = \operatorname{curl} \mathbf{A}$ is the magnetic field, Ψ is the order parameter, α and β are temperature dependent coefficients, and $e^* = 2e$ and $m^* = 2m$ are the charge and mass of a Cooper pair.

The variation of (2.2) with respect to Ψ * yields the usual equation for the order parameter:

$$-\alpha \Psi + \beta |\Psi|^{2} \Psi - \left(\nabla + \frac{ie^{*}}{\hbar c} \mathbf{A}\right)^{2} \Psi = 0, \qquad (2.3)$$

while the variation with respect to A leads to the equation

$$\operatorname{rot}\operatorname{rot}\mathbf{A} = \frac{4\pi}{c} (\mathbf{j}_{\star} + \mathbf{j}_{n}), \qquad (2.4)$$

where the current density standing on the right-hand side is the total current density $\mathbf{j} = \mathbf{j}_s + \mathbf{j}_n$, with

$$\mathbf{j}_s = \frac{\boldsymbol{e}^* \hbar}{2im^*} \left(\boldsymbol{\Psi}^* \nabla \boldsymbol{\Psi} - \boldsymbol{\Psi} \nabla \boldsymbol{\Psi}^* \right) - \frac{\boldsymbol{e}^{*2}}{m^* c} \mathbf{A} |\boldsymbol{\Psi}|^2.$$
(2.5)

Using (2.5), we can rewrite the expression (2.2) in the form³

$$\Phi_{s} = F_{s0} + \int_{V} \left\{ \frac{B^{2}}{8\pi} - \frac{1}{c} \mathbf{j}_{s} \mathbf{A} - \frac{1}{2} \frac{e^{*2}}{m^{*}c^{2}} A^{2} |\Psi|^{2} - \frac{1}{c} \mathbf{j}_{n} \mathbf{A} \right\} dv,$$
(2.6)

where

$$F_{*0} = F_{n0} + \int_{\mathbf{v}_{*}} \left\{ -\alpha |\Psi|^{2} + \frac{\beta}{2} |\Psi|^{4} + \frac{\hbar^{2}}{2m^{*}} |\nabla\Psi|^{2} \right\} dv; \qquad (2.7)$$

the integral term in (2.7) corresponds to the superconductorcondensation energy with allowance made for the order-parameter gradient. Using the chain of equalities

$$\int_{V_{\bullet}} \frac{\mathbf{B}^{2}}{8\pi} dv = \int_{V_{\bullet}} \frac{\mathbf{B}}{8\pi} \operatorname{rot} \mathbf{A} dv = \frac{1}{8\pi} \int_{V_{\bullet}} \{\operatorname{div} [\mathbf{A} \times \mathbf{B}] + \mathbf{A} \operatorname{rot} \mathbf{B} \} dv$$
$$= -\frac{H_{i}^{2}}{8\pi} V_{i} + \frac{1}{2c} \int_{V_{\bullet}} \mathbf{A} (\mathbf{j}_{\bullet} + \mathbf{j}_{n}) dv,$$

we can eliminate the field **B** from (2.6), and express everything in terms of the vector potential **A**:

$$\Phi_{s} = F_{s0} - \frac{1}{2} \frac{e^{s2}}{[m^{*}c^{2}} \int \mathbf{A}^{2} |\Psi|^{2} dv - \frac{1}{2c} \int \mathbf{Aj} dv$$

$$- \frac{1}{2c} \int \mathbf{Aj}_{n} dv.$$
(2.8)

Further, introducing the modulus and the phase of the order parameter, i.e., setting $\Psi = f e^{i\varphi}$, $f = |\Psi|$, and expressing **A** in terms of **j**_s and $\nabla \varphi$ with the aid of (2.5), we write (2.8), (2.5) in the form

$$\Phi_{s} = \tilde{F}_{s0} - \frac{1}{2c} \int \mathbf{A} \mathbf{j}_{n} \, dv + \frac{\hbar}{2e^{*}} \int \mathbf{j}_{s} \nabla \varphi \, dv, \qquad (2.9)$$

$$F_{s0} = \int_{V_s} \left\{ -\alpha f^2 + \frac{\beta}{2} f^4 + \frac{\hbar^2}{2m^*} (\nabla f)^2 \right\} dv + F_{n0}, \qquad (2.10)$$

$$\mathbf{j}_{\bullet} = \frac{e^{\bullet 2} f^{2}}{m^{\bullet} c} \left(-\mathbf{A} + \frac{\hbar c}{e^{\bullet}} \nabla \varphi \right).$$
(2.11)

The expressions (2.9)–(2.11) are exact, and are obtained from (2.2) and (2.5) by identity transformations; they are valid for our arbitrary dependence of Ψ (or f) and \mathbf{j}_n on the coordinates. Further, we limit ourselves to the consideration of the model case of a homogeneous superconducting cylinder, in which $f = |\Psi|$ does not depend on the coordinates, while j_n is given by (1.1) and does not depend on the angle coordinate θ .

It is well known that a hollow superconducting cylinder is a quantum system whose state is characterized by a whole number m that indicates how many flux quanta can be trapped in the cavity of the cylinder. (Flux quantization in hollow cylinders has been the subject of many papers, the recent ones among which are Refs. 17-20.) It is convenient to introduce the number *m* through the relation $\Psi = fe^{im\theta}$, where the phase φ of the wave function has been chosen (apart from unimportant vector-potential-gauge-dependent terms (see Refs. 1-10)) to be equal to $m\theta$, θ being the azimuthal coordinate: $0 \le \theta \le 2\pi$. The phase gradient in cylindrical coordinates can then be written in the form $\nabla \varphi = m/r$. We notice that, when the quantities $j_n = Q/r$ and $\nabla \varphi = m/r$ are substituted into (2.9), the factor 1/r is canceled by the factor r contained in the volume element $dv = 2\pi r dr$. Therefore, if we express A in (2.9) in terms of \mathbf{j}_s and $\nabla \varphi$ with the aid of (2.11), we are left in (2.9) with integrals of the type $I_s = \int j_s dr$, which are equal to the total superconducting current flowing around the cylinder. Further, taking account of the equality

$$I_{i} = I - I_{n} = \frac{c}{4\pi} (H_{i} - H_{in}), \quad H_{in} = \frac{4\pi}{c} I_{n}, \quad (2.12)$$

where $I = I_s + I_n$ is the total circumfluent current and H_1 is the resultant field in the cavity of the cylinder, we reduce, after simple transformations, the functional (2.9) to the form

$$\Phi_{s} = \tilde{F}_{s0} + \frac{\lambda^{2} H_{1n} \left(H_{1} - H_{1n} \right)}{4 \ln \left(r_{2} / r_{1} \right)} + \frac{m \Phi_{0}}{8\pi} \left(H_{1} - H_{1n} \right) - \frac{m \Phi_{0}}{8\pi} H_{1n}, \qquad (2.13)$$

where $\lambda^2 = m^* c^2 / 4\pi e^{*2} f^2$ (λ is the depth of penetration of the field into the superconductor). Within the framework of the model under consideration ($f = \text{const}, j_n = Q/r$), the

functional (2.13) is exact; it is expressed in terms of the as yet unknown quantity H_1 , the total field in the cavity of the cylinder.

§3. DETERMINATION OF THE FIELD H₁. ROLE OF THE QUANTUM LEVELS

To determine the field H_1 , we must turn to Eq. (2.4). In cylindrical coordinates, this equation has the form

$$\frac{d}{dr}\left[\frac{1}{r}\frac{d}{dr}(rA)\right] = \frac{1}{\lambda^2}\left(A - \frac{\hbar cm}{er}\right) - \frac{4\pi}{c}j_n; \qquad (3.1)$$

its general solution is

$$A = \frac{\hbar cm_{\text{eff}}}{e^{\prime}r} + aI_{1}\left(\frac{r}{\lambda}\right) + bK_{1}\left(\frac{r}{\lambda}\right),$$

$$B = \frac{1}{r}\frac{d}{dr}\left(rA\right) = \frac{1}{\delta}\left[aI_{0}\left(\frac{r}{\lambda}\right) - bK_{0}\left(\frac{r}{\lambda}\right)\right],$$
(3.2)

where I_n and K_n are Bessel functions of imaginary arguments, and we have set

$$m_{\rm eff} = m + \frac{H_{\rm in}\lambda^2}{\ln\left(r_2/r_{\rm i}\right)} \frac{2\pi}{\Phi_0}, \quad \Phi_0 = \frac{hc}{e^*}.$$

The arbitrary constant a and b are determined from the boundary conditions for the magnetic field:

$$B|_{r=r_1} = H_1, \quad B|_{r=r_2} = 0 \tag{3.3}$$

(the second condition in (3.3) corresponds to the absence of a field outside the cylinder). As a result, the solution (3.2) is expressed in terms of the field strength H_1 in the cavity. The condition

$$\oint_{r_1} \mathbf{A} d\mathbf{l} = \pi r_1^2 H_1$$

(the contour integral is taken along the inner surface of the cylinder and $\pi r_1^2 H_1$ is the magnetic flux in the cavity) gives us another equation from which the quantity H_1 can be determined. Finally, we shall have

$$H_{i} = \left(\frac{m\Phi_{0}}{\pi r_{i}^{2}} + H_{in}\frac{2\lambda^{2}}{r_{i}^{2}\ln(r_{2}/r_{i})}\right)\frac{D}{D_{i}};$$
 (3.4)

$$D = K_{0} \left(\frac{r_{1}}{\lambda}\right) I_{0} \left(\frac{r_{2}}{\lambda}\right) - I_{0} \left(\frac{r_{1}}{\lambda}\right) K_{0} \left(\frac{r_{2}}{\lambda}\right),$$

$$D_{i} = K_{2} \left(\frac{r_{1}}{\lambda}\right) I_{0} \left(\frac{r_{2}}{\lambda}\right) - I_{2} \left(\frac{r_{1}}{\lambda}\right) K_{0i} \left(\frac{r_{2}}{\lambda}\right).$$

(3.5)

Thus, the field in the cavity is known when the quantity H_{1n} and the value of m are known. Let us recall that the quantity H_{1n} varies with temperature according to (1.2). The penetration depth λ also depends on the temperature; therefore, the field H_1 in the cavity of the cylinder essentially depends on the temperature T (which in the adopted model corresponds to the temperature of the hot section of the thermoelectric circuit). At $T = T_c$, the penetration depth is infinite, i.e., λ ($T = T_c$) = ∞ , the order parameter vanishes, i.e., $f(T = T_c) = 0$, and the field $H_1 = H_{1n}^0$.

Substituting the obtained expression (3.4) for H_1 into (2.13), we obtain the system's thermodynamic potential expressed as a function of the temperature. It is convenient to introduce the difference between the functionals

$$\delta \Phi = \Phi_s(T) - \Phi_0, \qquad (3.6)$$

where $\Phi_0 = \Phi_s(T = T_c) = \Phi_s|_{f=0}$ is the thermodynamic potential of the system when the order parameter is equal to zero, i.e., when the cylinder is in the normal state. If $\delta \Phi < 0$, this indicates that the superconducting state is favored (i.e., possesses a lower energy), but if $\delta \Phi > 0$ it is advantageous for the system to go over into the normal state. Determining the quantity $\delta \Phi$ with the aid of (3.6), (2.13), and (3.4), we obtain, after obvious transformations, the expression

$$\delta \Phi = \Phi_{s0} + \frac{\Phi_0}{8\pi} \frac{\Phi_0}{\pi r_1^2} \frac{D}{D_1} \left[m - p \frac{\pi r_1^2 H_{1n}}{\Phi_0} \right]^2 + q \frac{\pi r_1^2 H_{1n}^2}{8\pi}, \qquad (3.7)$$

where $\Phi_{s0} = V_s \{ -\alpha f^2 + \frac{1}{2}\beta f^4 \}$, $V_s = \pi (r_2^2 - r_1^2)$ being the volume occupied by the superconductor (we assume that the length of the cylinder along the z axis is equal to unity). The quantities D and D₁ are defined in (3.5),

$$p = \frac{D_{i}}{D} - \frac{2\lambda^{2}}{r_{i}^{2}\mathscr{D}}, \quad \mathscr{L} \equiv \ln \frac{r_{2}}{r_{i}},$$

$$q = p_{0} - p, \quad p_{0} = \left(\frac{d}{r_{i}} + \frac{d^{2}}{2r_{i}^{2}} - \mathscr{L}\right) / \mathscr{L}^{2}$$
(3.8)

(here p_0 is the value of p when f = 0). When f = 0, the quantity $\delta \Phi = 0$.

Finally, introducing in place of $f = |\Psi|$ the reduced order parameter ψ with the aid of the relations¹²⁻¹⁴

$$\psi = \frac{f}{f_{\rm c}}, \quad f_{\rm o}^2 = \frac{\alpha}{\beta}, \quad H_{cm} = \left(\frac{4\pi\alpha^2}{\beta}\right)^{\prime \prime_{\rm o}} = \frac{\Phi_{\rm o}}{2\pi\sqrt{2\xi(T)}\delta_L(T)},$$

$$\xi^2(T) = \frac{\hbar^2}{2m^*\alpha}, \quad \delta_L^2(T) = \frac{m^*c^2}{4\pi e^* f_{\rm o}^2(T)}, \quad \lambda = \frac{\delta_L(T)}{\psi},$$

(3.9)

we write (3.7) and (3.4) in the following final form

$$\mathcal{F} = \frac{\delta \Phi}{V_s H^2_{cm}/8\pi} = -2\psi^2 + \psi^4 + \frac{8\xi^2(T) \,\delta_L^2(T)}{(r_2^2 - r_1^2) \,r_1^2} \\ \times \left[\frac{D}{D_1} (m - ph_{1n})^2 + qh_{1n}^2\right]; \qquad (3.10)$$

$$h_{i} = \left(m + \frac{2\lambda^{2}}{r_{i}^{2}\mathscr{D}}h_{ini}\right)\frac{D}{D_{i}}, \quad h_{i} = \frac{\pi r_{i}^{2}H_{i}}{\Phi_{0}}, \quad h_{in} = \frac{\pi r_{i}^{2}H_{in}}{\Phi_{0}}.$$
(3.11)

The functional \mathcal{F} , (3.10), describes the behavior of the system studied by us as a function of the temperature, and will be investigated in detail below. But certain important characteristics of the behavior of this system can already be seen from the expression (3.10). Indeed, we assume, as is usually done in the investigation of thermoelectric phenomena in superconductors, that m = 0, i.e., that there is initial-

ly no frozen flux inside the cylinder (the field $h_1 = 0$ when $T = T_1$). The switching on of the normal current j_n , i.e., the establishment of the field $h_{1n}(T > T_1)$, leads to the appearance in (3.10) of the large positive contribution proportional to $p^2 h_{1n}^2$, which quickly makes the state with m = 0 thermodynamically unstable, i.e., $\mathcal{F} > 0$ (let us recall that $h_{1n}^{(0)}$ in (1.2) is of the order of 0.1–1 G, the characteristic values of $h_{1n}^{(0)}$ are of the order of 10³-10⁷ for $r_1 \sim 0.1-1$ cm, i.e., $h_{1n}^{(0)} \ge 1$; the quantity p in (3.10) is of the order of unity, and the quantity q is small (see below)). Since it is advantageous for the system to be in the state with the minimum value \mathcal{F} , it can, when the quantity h_{1n} attains a value $h_{1n} \approx \frac{1}{2}$, go over into the state with m = 1, thereby lowering its total energy. As the temperature is raised further, and $h_{1n}(T)$ increases, it becomes energetically advantageous for the system to undergo $m \rightarrow m + 1$ transitions into states with higher and higher values of m. These transitions (which occur at $h_{1n} \approx m + \frac{1}{2}$ minimize the term in (3.10) proportional to $(m - ph_{1n})^2$, which is always $\leq \frac{1}{4}$. The presence of the small parabolic qh_{1n}^2 term in (3.10) gives rise to a situation in which the positive contribution of this term can, as h_{1n} increases, so exceed the energy of the system that the superconducting state becomes disadvantageous ($\mathcal{F} > 0$), and the system has to go over into the normal state. Thus, the superconducting state cannot exist at very large h_{1n} (or j_n). An important feature of the above-described picture is the conclusion that the normal component of the thermoelectric current in the superconducting ring can induce spontaneous transitions into states with large m, which correspond to large numbers of flux quanta trapped in the ring, even in the absence of an external magnetic field. As can be seen from (3.11), the appearance of large *m* leads to an additional increase in the internal field h_1 , and this allows us to hope that we can describe the experimentally observed giant thermoelectric effect as being the result of such transitions. A more detailed investigation of this question is carried out below. But let us note the following here.

Qualitatively, the described behavior of a hollow superconducting cylinder in the presence of a prescribed normal current j_n is entirely similar to the behavior of a hollow superconducting cylinder located in an external magnetic field H_0 parallel to the axis of the cylinder. This system has been investigated in a number of papers. In particular, the $m \rightarrow m + 1$ transitions that occur in an external field between the quantized levels are investigated in detail in Refs. 17–19. The oscillations, connected with these transitions, of the sample's critical temperature as a function of the external field H_0 have been experimentally observed, $^{21-23}$ and so have transitions between levels with different m.²⁴⁻²⁶

A great similarity between these two cases is clearly revealed when we compare (3.10) and (3.11) with the corresponding expressions for a cylinder in an external field:⁴⁾

$$\mathcal{F} = \psi^{4} - 2\psi^{2} + \frac{8\xi^{2}(T)\delta_{L}^{2}(T)}{r_{1}^{2}(r_{2}^{2} - r_{1}^{2})} \left\{ \frac{D}{D_{1}} [m - \tilde{p}h_{0}]^{2} + \tilde{q}h_{0}^{2} \right\}; \quad (3.12)$$

$$h_{1} = \left(m + \frac{2\lambda^{2}}{r_{1}^{2}D}h_{0} \right) \frac{D}{D_{1}}, \quad h_{1} \equiv \frac{\pi r_{1}^{2}H_{1}}{\Phi_{0}}, \quad h_{0} \equiv \frac{\pi r_{1}^{2}H_{0}}{\Phi_{0}},$$

$$\tilde{p} = \frac{D_{1}}{D} - \frac{2\lambda^{2}}{r_{1}^{2}D}, \quad \tilde{q} = \frac{4/\rho_{1}^{2} - D_{1} - D_{2}}{D}.$$

$$(3.13)$$

Here H_1 is the field in the cavity, H_0 is the external field,

 $\lambda^2 = \delta_L^2 / \psi^2$, $\rho_1^2 = r_1^2 / \lambda^2$, $\rho_2^2 = r_2^2 / \lambda^2$,

the quantities D and D_1 are defined in (3.5), and

 $D_2 = K_2(\rho_2) I_0(\rho_1) - I_2(\rho_2) K_0(\rho_1).$

We see that the formulas (3.10) and (3.11) with h_{1n} replaced by h_0 respectively coincide with (3.12) and (3.13) up to small differences in the parameters p and q, which characterize the screening properties of the system. Thus, the normal component of the thermoelectric current (i.e., the quantity h_{1n} in (3.10)) plays the role of the external field h_0 in (3.12), the problem of determining the total thermoelectric flux in the system in the case of a prescribed j_n does not differ essentially from the problem of finding the field inside the cavity of the cylinder in a prescribed external field h_0 . This similarity further justifies the viewpoint, expressed in the Introduction, that the thermoelectric effect has essentially an electrodynamic (Meissner-type) character. Moreover, the important role of the phase factor $e^{im\theta}$, which is evidently due to a purely geometrical factor (i.e., to the fact that the system is doubly connected), and is in no way connected with the temperature gradient, is now clear.

§4. DETERMINATION OF *h*1 AS A FUNCTION OF THE TEMPERATURE. HYSTERESIS

The functional \mathscr{F} , (3.10), depends on the temperature and the reduced order parameter ψ . According to the Ginzburg-Landau theory of superconductivity,¹²⁻¹⁴ the parameter ψ for a given temperature should be determined from the condition for a minimum of the functional: $\partial \mathscr{F} / \partial \psi = 0$. The ψ value obtained from here should be substituted into (3.11) (let us recall that $\lambda = \delta_L(T)/\psi$), after which the field strength h_1 inside the cylinder is determined as a function of the temperature. In the general case this program requires the performance of rather tedious numerical computations. In a number of limiting cases the problem gets simplified.

We shall be particularly interested in the case of a thickwalled superconducting cylinder, when the following inequalities are valid:

$$\rho_1 = \psi r_1 / \delta_L(T) \gg 1, \quad \Delta = \psi d / \delta_L(T) \gg 1,$$

$$d = r_2 - r_1, \quad d / r_1 \ll 1.$$

Using the expansions of the Bessel functions for large values of the arguments, we find

$$D/D_{1} = 1 - 2/\rho_{1} + 3/\rho_{1}^{2}, \quad D_{1}/D = 1 + 2/\rho_{1} + 1/\rho_{1}^{2},$$

$$p_{0} = 1 + \frac{2}{3}d_{1}, \quad p = 1 + 2/\rho_{1} - (2 - d_{1})/\rho_{1}^{2}d_{1}, \quad (4.1)$$

$$q = p_{0} - p = \frac{2}{3}d_{1} - \frac{2}{\rho_{1}} + (2 - d_{1})/\rho_{1}^{2}d_{1}, \quad d_{1} = d/r_{1} \ll 1.$$

Substituting these expansions into (3.10) and (3.11), and taking into account the terms $\sim 1/\rho_1^2$, we obtain

$$\mathcal{F} = -2\psi^{2} + \psi^{4} + \frac{4\xi^{2}(T)\delta_{L}^{2}(T)}{r_{i}^{3}d} \left\{ c_{0} + \frac{c_{1}}{\psi} + \frac{c_{2}}{\psi^{2}} \right\},$$

$$c_{0} = (m - h_{1n})^{2} + \frac{2}{3}d_{1}h_{1n}^{2}, \quad c_{1} = -2m^{2}\delta_{L}(T)/r_{1},$$

$$(4.2)$$



FIG. 1. Dependence of h_1 on $t = T - T_1$ for pure In: $\kappa = 0.2$, $h_{1n}(0) = 10^5$, $r_1 = 0.6$ cm, d = 0.02 cm, $\xi_0 = 3 \times 10^{-5}$ cm, $T_1 = 4.000$ K, and $T_c = 4.007$ K. The dashed curve is the experimental curve obtained by van Harlingen *et al.*⁸

$$c_{2} = -\frac{\delta_{L}^{2}(T)}{r_{1}^{2}} \left[\frac{2h_{1n}}{d_{1}} (\hat{h}_{1n} - 2m) - 3m^{2} \right];$$

$$h_{1} = \left[m + \frac{2\delta_{L}^{2}(T)}{r_{1}d} \frac{h_{1n}}{\psi^{2}} \right] / \left[1 + \frac{2\delta_{L}(T)}{r_{1}\psi} + \frac{\delta_{L}^{2}(T)}{r_{1}^{2}\psi^{2}} \right]. \quad (4.3)$$

It is easy to find the condition $\partial \mathcal{F} / \partial \psi = 0$ for a minimum of the functional (4.2), determine from it the value $\psi_0 = \psi(T)$, and then find $h_1(T)$. In Fig. 1 the continuous curves depict the dependence $h_1(T)$ in the m = 0, m = 100, m = 200, and m = 300 states for pure In [see the formulas (1.3)] with $x_p = 0.2$. The other parameters are indicated in the caption for Fig. 1, and correspond to the actual conditions of the experiment of van Harlingen et al.,8 which corresponds most closely to the cylindrical-sample model being considered by us. The dashed curve shows the $h_1(T)$ dependence found by van Harlingen et al.8 The open circles on the theoretical curves indicate the points where the minimum of the functional \mathscr{F} passes through zero: $\mathscr{F}(\psi_0) = 0, \ \mathscr{F}'(\psi_0) = 0$. The crosses indicate the points where the minima of ${\mathscr F}$ disappear, being replaced by a point of inflection: $\mathscr{F}'(\psi_{00}) = 0$, $\mathscr{F}''(\psi_{00}) = 0$. In the temperature range between the points ψ_0 and ψ_{00} we have $\mathscr{F}_{\min}(\psi) > 0$, i.e., a state with a given *m* is metastable against the transition into the normal state. A solution with a given *m* terminates at the point ψ_{00} , and a transition into a state with a higher m, or into the normal state, should necessarily occur.

Figure 2 shows the analogous curves for extremely dirty In with $\kappa_d = 20 \ [l = 3 \times 10^{-7} \text{ cm}; \text{ see (1.4)}]$. It can be seen



FIG. 2. Dependence of h_1 on $t = T - T_1$ for extremely dirty In: $\kappa = 20$, $l = 3 \times 10^{-7}$ cm. The remaining parameters are the same as in Fig. 1.

that the contamination of the sample leads to a significant enhancement of the effect, which is due to an increase in the penetration depth $\delta_L(T)$.

We should, in discussing the results presented in Figs. 1 and 2, bear in mind that a comparison of the theory with experiment can be carried out only conditionally. The effect depends strongly on the geometric dimensions, on the presence of impurities in the sample, and on $H_{1n}^{(0)}$. An actual experiment is performed on an inhomogeneous sample, which may also be important (role of the inhomogeneity will be discussed in greater detail in §6). But some qualitative features can already be seen from Figs. 1 and 2. Since the experimental curve clearly lies above the theoretical curve corresponding to the state with m = 0, we can draw the conclusion that transitions to higher-lying m > 0 levels are apparently realized in experiment. This prediction of the theory can, in principle, be experimentally verified. Indeed, so long as the system at $T > T_1$ is in the m = 0 state, the state changes with temperature reversibly; in particular, we return to the $h_1 = 0$ state when the temperature decreases to $T = T_1$. But if the transition was into an $m \neq 0$ state, we return to another state $h_1 = m$ when the system cools down to $T = T_1$. These hysteresis transitions are arbitrarily marked in Figs. 1 and 2 by arrows.

The thermodynamic theory constructed above cannot predict the temperature at which the jump from the m into the m + 1 state occurs. It only indicates the limits of the temperature interval within which such a jump can occur. Figure 3 schematically shows on an enlarged scale the dependences $h_1(T)$ with allowance for the possible $m \rightarrow m + 1$ transitions. The stepped curve (a) corresponds to the transitions that occur when the system consistently chooses the lowest energy state. These transitions occur at half-integer values of $h_{1n} = m + \frac{1}{2}$ [in other words, the curve (a) corresponds to thermodynamic-equilibrium transitions]. Thus, under conditions of thermodynamic equilibrium, the dependence $h_1(T)$ has the form of the curve (a), and moreover $h_1(T) \approx h_{1n}(T)$. Let us note that, in the case of a hollow cylinder located in an external field, the situation with $h_1 \approx h_0$, i.e., the situation in which the external field penetrates fully into the cavity, corresponds to the state in which the energy has its minimum value. This indicates that the states with $m \neq 0$ in the case when $h_0 = 0$ (i.e., the states with frozen-in



FIG. 3. Schematic level-to-level transition curves as determined by: a) the energy minimum; b) the points where the fluctuation barrier disappears; c) the points where $\mathscr{F}' = 0$, $\mathscr{F}_{\min} = 0$; d) the points where the solutions terminate, i.e., where $\mathscr{F}' = 0$, $\mathscr{F}'' = 0$. The continuous curve is an experimental curve; the dotted curve corresponds to the case m = 0, $\psi = 1$.



FIG. 4. Schematic drawing of the fluctuation barriers; $\langle \chi \rangle$ is an arbitrary parameter of the fluctuations.

flux) cannot be realized under equilibrium conditions. But we know that this is, in fact, not the case: Such states are quite stable and exist for indefinitely long periods of time, even though they are metastable, i.e., energetically disadvantageous. In other words, under real conditions the system does not go after the lowest energy states.

If the system went after the states in which the functional $\mathcal{F}_{min} = 0$ (the energies of the superconducting and normal states are equal in this case), the transitions would proceed along the stepped curve c) in Fig. 3 (see also the open circles in Figs. 1 and 2). Finally, if the system underwent a transition every time the value $\partial^2 \mathcal{F} / \partial \psi^2 = 0$ was attained (i.e., at every one of the inflection points of the functional, which correspond to the termination of the superconducting solutions of a given number m), the transitions would occur at the points marked by crosses in Fig. 1.

The stepped curve b) in Fig. 3 is in full accord with the $h_1(t)$ dependence actually observed in experiment. In order to describe this dependence theoretically, we need to find out the energy principle governing the $m \rightarrow m + 1$ transitions (or the jumps $m \rightarrow m + n$ over several steps at one stroke). This can be done with the aid of arguments connected with the fluctuations in the superconductor.

Indeed, we can imagine in the spirit of the theory of fluctuations that the minima of the functional \mathcal{F} at a given temperature T are separated by fluctuation barriers (see Fig. 4), and that the barrier between the states m and m + 1 needs only to be overcome for the $m \rightarrow m + 1$ transition to occur. The theoretical estimation of the height of the fluctuation barriers (and, thus, the description of the experimentally observed dependence $h_1(T)$ constitutes a separate problem requiring special treatment. Here we limit ourselves to these qualitative remarks, and emphasize the fact that special experiments need to be performed in order to elucidate the presence of hysteresis effects in thermoelectric phenomena occurring in superconductors, as well as to study them in detail. Let us note that, in view of the obvious likeness of the thermoelectric phenomena and the behavior of a hollow cylinder located in an external field, it would have been interesting to perform a more detailed investigation of the hysteresis effects (in particular, the character of the transitions between the quantum levels at $T \rightarrow T_c$) in a thick hollow cylinder in an external field. This would have enabled us to obtain an independent estimate for the height of the fluctuation barrier, which, apparently, is the same for both systems.

Let us, in conclusion of this section, note that, according to the theory, there exists in the vicinity of T_c some tem-

perature T_c^* (determined by the condition $\mathscr{F}_{\min} = 0$, or $\partial^2 \mathcal{F} / \partial \psi^2 = 0$, or the condition for the vanishing of the fluctuation barrier) at which the superconducting solutions vanish. This means that the transition into the normal state, as characterized by the complete penetration of the field (i.e., by the equality $h_1 = h_{1n}$), should, as the ring is heated, occur not at T_c , which is characteristic of the super-conductor in zero field, but at $T_c^* < T_c$. This effect is a direct consequence of the interdependence of the order parameter ψ and the field h_{1n} , that arises in the Ginzburg-Landau theory, and is described by the nonlinear functional $\mathscr{F}(\psi_1, h_{1n})$. (Dependences of this type are well known, and appear in the case of a superconductor located in an external field in the dependence of the penetration depth $\lambda = \delta_L(T)/\psi$ on the field.²⁷) In the simple London theory (which corresponds to the case $\psi = 1$) the superconducting state would have survived right up to $T = T_c$ (the theoretical dependence $h_1(T)$ for $\psi = 1$ is schematically depicted in Fig. 3 by the dotted line [cf. Ref. 10]]. The strong effect of h_{1n} on ψ at $T \rightarrow T_c$ is not surprising, since, as $T \rightarrow T_c$, the thermodynamic field $H_{cm}(T)$ tends to zero, while $H_{1n}(T)$ increases, so that there certainly exists some $T_c^* < T_c$ at which H_{1n} becomes higher than H_{cm} and the suppression of the superconductivity occurs. In Figs. 1 and 2 we show the $h_1(T)$ curve obtained experimentally by van Harlingen et al.8

§5. THE TRANSITIONS FROM THE NORMAL INTO THE SUPERCONDUCTING STATE

Another example illustrating the hysteretic behavior of the system under investigation is the transition of the thermoelectric ring into the superconducting state when it is cooled from a temperature $T > T_c$. To illustrate the agruments presented below, we schematically depict in Fig. 5 the behavior of $\mathcal{F}(\psi)$, (3.10), in the entire interval of variation of ψ : $0 \le \psi \le 1$. At low temperatures ($T \approx T_1$, the curve 1) the minimum of the potential occurs at $\psi \approx 1$, and is marked by a circle on the curve. As the temperature is raised (the curves 2-6), the minimum rises; the curve 4 corresponds to the equilibrium-transition point $\mathcal{F} = 0$, $\mathcal{F}' = 0$; the cross on the curve 5 marks the termination point for the superconducting solutions: at higher temperatures the potential has a minimum only at $\psi = 0$. If we start from a point in the hightemperature region (the curve 6), the system will initially be at the point $\psi = 0$, and will remain in the normal state until the temperature drops so much (the curve 4) that the minima becomes $\mathcal{F}_{\min} < 0$: transitions into the superconducting



FIG. 5. Schematic plots of $\mathcal{F}(\psi)$ for different temperatures.

state with $\psi \neq 0$ become possible at this temperature. But as long as there is a barrier (the peak in the curve 3) between the superconducting and the normal states, the system can remain in the $\psi = 0$ state ("supercooled" normal state). The curve 2 corresponds to the temperature at which the peak in the curve 3 disappears, and there are no other solutions except the superconducting ones with $\psi \approx 1$. The curve 2 corresponds to the conditions $\partial \mathcal{F} / \partial \psi|_{\psi=0} = 0$, $\partial^2 \mathcal{F} / \partial \psi^2|_{\psi=0} = 0$ (the supercooling limit).

To find the temperature T_{sc} corresponding to the curve 2, we must have the expression for \mathcal{F} in the limit $\psi \ll 1$. Using the Bessel-function expansions for small values of the arguments, we find up to the terms $\sim \psi^4$ the expression

$$\mathcal{F} = -2\psi^{2} + \psi^{4} + \frac{2\xi^{2}(T)}{r_{i}^{2}}\psi^{2}\left\{\left(1 - \frac{r_{i}d}{2\delta_{L}^{2}}\psi^{2}\right)(m - \tilde{p}h_{in})^{2} + \tilde{q}h_{in}^{2}\right\},\$$

$$\tilde{p} = 1 - \frac{2}{45}d_{i}^{3}\rho_{i}^{2} + \frac{1}{32}d_{i}^{3}\rho_{i}^{4}, \quad \tilde{q} = \frac{4}{45}d_{i}^{2} - \frac{1}{16}d_{i}^{2}\rho_{i}^{2},$$

$$\rho_{i} = \frac{r_{i}}{\delta_{L}(T)}\psi, \quad d_{i} = \frac{d}{r_{i}},$$
(5.1)

which can be represented in the form $\mathscr{F} = a\psi^2 + b\psi^4$, where

$$a = -2 + \frac{2\xi^{2}(T)}{r_{i}^{2}} \left[(m - h_{in})^{2} + \frac{4}{45} d_{i}^{2} h_{in}^{2} \right],$$

$$b = 1 - \kappa^{-2} \left[d_{i} (m - h_{in})^{2} + \frac{1}{8} d_{i}^{2} h_{in}^{2} + \frac{8}{45} d_{i}^{3} h_{in} (h_{in} - m) \right]$$
(5.2)

[we have also used the approximation $d_1 = d/r_1 \leqslant 1$ in the formulas (5.1) and (5.2)]. The condition $\mathscr{F}' = 0$ gives $\psi_{ext}^2 = -a/2b$, the maximum point on the curve 3, and the condition $\mathscr{F}'' = 0$ yields $\psi_{inf}^2 = -a/6b$, the point of inflection of the curve 3 in the region $\psi \leqslant 1$. These points merge (the curve 2) when a = 0, which provides an equation for the determination of the temperature (with allowance for the fact that $m = h_{1n}$ at the point T_{sc} :

$$\frac{4}{45}d_1^2 h_{1n}^{(0)2} \left(1 - \frac{\tau}{\tau_1}\right)^2 = \frac{\tau_1^2}{\overline{\xi}_0^2}\tau.$$
(5.3)

Here $\tau = 1 - T/T_c$ and $\tau_1 = 1 - T_1/T_c$; $\overline{\xi}_0 = 0.74 \, \xi_0$ in the case (1.3) of pure materials and $\overline{\xi}_0 = 0.85 \, (\xi_0 l)^{\frac{1}{2}}$ in the dirty case (1.4). Hence

$$\frac{\tau}{\tau_{i}} = 1 + \frac{1}{2Y} [1 + (1 + 4Y)^{\frac{1}{5}}], \quad Y = \frac{4}{45} \frac{\bar{\xi}_{0}^{2}}{r_{i}^{2}} \frac{d^{2}}{r_{i}^{2}} \frac{h_{in}^{(0)2}}{\tau_{i}}; \quad (5.4)$$

for $Y \ll 1$ we have

$$1 - \frac{T_{sc}}{T_c} = \frac{4}{45} \frac{\bar{\xi}_0^2}{r_1^2} \frac{d^2}{r_1^2} h_{1n}^{(0)2} .$$
 (5.5)

The transition temperatures T_c are indicated on the curves in Figs. 1 and 2. In the pure case $1 - T_{sc}/T_c \sim 10^{-3}$; in the dirty, $1 - T_{sc}/T_c \sim 10^{-5}$.

In Fig. 6 we schematically show the paths followed by the system in different temperatures regimes. On being heated from $T = T_1$, the system follows the path 1–2–3–4; if cooling is started at the point 2, the system will proceed along the



FIG. 6. Possible paths in different temperature regimes.

line 2–5, in accordance with the value $m = m_2$ at the point 2 (or along the line 3-7 if the cooling is started at the point 3). When cooled from the normal state, the system should follow the line 4–3–6–8. The point 6 corresponds to the absolute limit (5.3) of the "supercooled" state; but actually the system can go over into the superconducting state at some intermediate point 9 (corresponding to the curve 3 in Fig. 5) in Fig. 6, and then the path 4-3-9-10 may be realized during the cooling. The transition of the system from the normal into the superconducting state at the point 9 is clearly caused by the fluctuation effects, and is a result of the overcoming of the fluctuation barrier. In Fig. 6 we can, above all, see that there exists a superconducting-normal state transition point $T_c^* < T_c$, due, possibly, to the fluctuations (see Sec. 4). Thus, the study of the hysteresis transitions, including the transitions from the normal into the superconducting state, is of definite interest, and can provide valuable physical information about the fluctuations connected with the transitions between the quantum levels in a microscopic toroidal superconducting system.

§6. THE INHOMOGENEOUS CASE

The theory above describes the behavior of a homogeneous hollow cylinder with a prescribed normal current in the superconductor. Under real experimental conditions,⁸ the thermoelectric ring is highly inhomogeneous [see Fig. 7(a)], a fact which should be taken into account in a comparison of the predictions of the theory with experiment. According to the viewpoint adopted in the present paper, the purely electrodynamic aspects essentially predominate in the thermoelectric phenomena. Therefore, of greatest importance in the investigation of the heterogeneous ring is the fact that the superconductors a and b can have significantly different London lengths $\delta_{La, b}$ and wall thicknesses (see Fig. 7). This means that there is in the ring a weak spot [indicated in Fig. 7(a) by the arrow] where the fluctuation processes should primarily occur and result in the field's penetrating into the ring and the system's going over to the quantum level m. Such processes are facilitated in the heterogeneous ring, since they do not engulf the whole volume of the superconductor (as happens in the homogeneous case), but are localized at the weak spot.

To describe the heterogeneous system, we consider a ring, shown in Fig. 7(c), with inside radius $r_{1a} = r_{1b} = r_1$, outside radii r_{2a} and r_{2b} and, consequently, London lengths $\delta_{La}(T)$ and $\delta_{Lb}(T)$, and order parameters ψ_a and ψ_b . Let us

FIG. 7. a) Schematic drawing of a real heterogeneous sample, according to Ref. 8; b) plot of the function $\delta_{La}(x)$; c) the heterogeneous model. $S \approx 1$ cm², d = 0.02 cm.

assume that the total normal current, or, equivalently, a field H_{1n} that depends linearly on the temperature according to (1.2), is prescribed in this ring. As in the homogeneous model, the temperature T is the same for the entire ring. Let the angular dimensions of the superconductors a and b be θ_a and θ_b , where, in units of 2π , $\theta_a + \theta_b = 1$. It is clear that the field distribution and the total current inside each of the superconducting sections θ_a and θ_b of the heterogeneous ring are given by the formulas obtained in §3 for the homogeneous model. It is not difficult to verify that the field in the cavity in the heterogeneous case is given by a formula similar to (3.4) (as in the homogeneous case, we assume that $f_a = \text{const}$, $f_b = \text{const}$):

$$H_{1} = \left(\frac{m\Phi_{0}}{\pi r_{1}^{2}} + H_{1n}\frac{2\lambda_{\text{eff}}^{2}}{r_{1}^{2}}\right)\frac{1}{Z_{\text{eff}}},$$

$$Z_{\text{eff}} = \theta_{a}\cdot\frac{D_{1}^{(a)}}{D^{(a)}} + \theta_{b}\frac{D_{1}^{(b)}}{D^{(b)}},$$

$$\lambda_{\text{eff}}^{2} = \theta_{a}\frac{\lambda_{a}^{2}}{\mathscr{L}_{a}} + \theta_{b}\frac{\lambda_{b}^{2}}{\mathscr{L}_{b}},$$

$$\mathscr{L}_{a} = \ln\frac{r_{2a}}{r_{1a}}, \qquad \mathscr{L}_{b} = \ln\frac{r_{2b}}{r_{1b}},$$
(6.1)

the quantities D and D_1 are defined in (3.5); the indices a and b indicate the superconductors to which the corresponding quantities pertain.

It is convenient, in determining the thermodynamic potential of the heterogeneous system, to proceed from the formula (2.9), which is valid in the general case. Further, proceeding in much the same way as in the homogeneous case, we obtain a formula of the type (2.13):

$$\Phi_{s} = \tilde{F}_{s0}^{(a)} \theta_{a} + \tilde{F}_{s0}^{(b)} \theta_{b} + \frac{\lambda_{eff}^{2}}{4} H_{in} (H_{i} - H_{in}) + \frac{m \Phi_{0}}{8\pi} (H_{i} - H_{in}) - \frac{m \Phi_{0}}{8\pi} H_{in}.$$
(6.2)

Here the $\tilde{F}_{s0}^{(a, b)}$ are given by formulas similar to the formula (2.10). Let us now introduce, as in (3.6), the difference

$$\delta \Phi = \Phi_s - \Phi_0, \quad \Phi_0 = \Phi_s|_{f_0 = 0}; \tag{6.3}$$

the quantity $\delta \Phi$ is convenient in the sense that it immediately shows which of the states of the system is energetically more advantageous: if $\delta \Phi < 0$, then the fully superconducting state with order parameters $f_a \neq 0$, $f_b \neq 0$ is advantageous; if, on the other hand, $\delta \Phi > 0$, then the transition into the state with $f_a = 0$, i.e., the transition of the weaker superconductor a ($T_{ca} < T_{cb}, \delta_{La} > \delta_{Lb}$) into the normal state, is

advantageous. We shall further assume that δ_{Lb} and f_b do not depend on the temperature $(T \ll T_{cb})$. Repeating the calculations that led to the formula (3.7), we find in the heterogeneous case that

$$\delta \Phi = \theta_a \Phi_{s_0}^{(a)} + \frac{\Phi_0}{8\pi} \frac{\Phi_0}{\pi r_i^2} \left[m - p_{\text{eff}} \frac{\pi r_i^2 H_{in}}{\Phi_0} \right]^2 \frac{1}{Z_{\text{eff}}} + q_{\text{eff}} \frac{\pi r_i^2 H_{in}^2}{8\pi}; \qquad (6.4)$$

$$p_{\text{eff}} = \theta_{a} \frac{D_{i}^{(a)}}{D^{(a)}} + \theta_{b} \frac{D_{i}^{(b)}}{D^{(b)}} - \frac{2\lambda_{\text{eff}}^{2}}{r_{1}^{2}},$$

$$q_{\text{eff}} = p_{\text{eff}} |_{f_{a}=0} - p_{\text{eff}} = \theta_{a} q^{(a)}.$$
(6.5)

Finally, going over to the reduced units (3.9), we obtain formulas similar to (3.10) and (3.11):

$$\mathcal{F} = \frac{\delta \Phi}{\theta_a V_s^{(a)} H_{cm(a)}^2 / 8\pi} = -2\psi_a^2 + \psi_a^4 + \frac{8\xi_a^2(T)\delta_{La}^2(T)}{(r_{2a}^2 - r_{1a}^2)r_{1a}^2} \left[\frac{(m - p_{\text{eff}}h_{1n})^2}{\theta_a Z_{\text{eff}}} + q^{(a)}h_{1n}^2\right], \quad (6.6)$$

$$V_s^{(a)} = \pi (r_{2a}^2 - r_{1a}^2), \quad h_1 = \left(m + \frac{2\lambda_{\text{eff}}^2}{r_1^2} \right) \frac{1}{Z_{\text{eff}}}.$$
 (6.7)

An important characteristic of the formula (6.6), as compared with (3.10), is the presence of the factor $1/\theta_a$ in the square brackets in (6.6), a factor which is large for $\theta_a \ll 1$. As can be seen from a comparison of (6.4) with (6.6), this factor is connected with the fact that the condensation energy $\theta_a \Phi_{s0}^{(a)}$ (which is negative and guarantees the stability of the superconducting state) in (6.4) in the heterogeneous case is θ_a times smaller than the corresponding energy in the homogeneous case, since the superconductor-normal metal transition now effects only a fraction θ_a of the entire volume of the superconductor. Therefore, the nonlinear field effects [which are proportional to the quantity standing in the square brackets in (6.6)] play a greater role in the heterogeneous superconductor. Figure 8 illustrates the effect of the heterogeneity on the field h_1 in the thermoelectric ring.

In conclusion of this section, let us make the following remark. The formulas (6.1)–(6.7) for the heterogeneous case are approximate, since they were derived without allowance for the fact that the total current **j** in the vicinity of a soldered joint has, besides the component j_{θ} , a component j_{r} in the radial direction (which is connected with the difference in



FIG. 8. The dependence $h_1(T)$ for the homogeneous (1) and inhomogeneous (2) models; $\theta_a = 1/5$. The remaining parameters are the same as in Fig. 1.

the London lengths δ_{La} and δ_{Lb}). The consistent allowance for this effect would have required the solution of the partial differential equation (2.4) for the two-variable function $\mathbf{A}(r, \theta)$, which is a complicated mathematical problem. In the approximation adopted by us, the component j_r is neglected everywhere, which allows us to directly use the formulas obtained for the homogeneous case. It is evident that the role of the effects connected with the soldered joints is minor, especially as we are interested only in the strength of the total circumfluent current (or the resultant field in the cavity), which does not depend on the presence of the component j_r . Let us note that a similar method is used in Ref. 10 to investigate the thermoelectric effect in a system with a somewhat different geometry.

§7. CONCLUSION

The main result of the above-performed investigation is the conclusion that there is a profound similarity between the behavior of a thermoelectric system and the behavior of a superconducting hollow cylinder in an external field. Characteristic of both systems is the presence of a topological singularity-a cavity-as a result of which each of these two doubly connected systems is characterized by a quantum number m that indicates how many quanta of flux $m\Phi_0$ can be contained in the cavity. The role of external field H_0 is played in the case of the thermoelectric ring by the externally prescribed normal-excitation current I_n . As the I_n in the thermoelectric circuit increases, it becomes possible for spontaneous transitions to levels with m > 0 to occur even when the external field $H_0 = 0$ and the system was initially in the state with m = 0. Accordingly, it is quite probable that the experimentally observed⁸ "giant" thermoelectric effect can be explained as being the result of the level-to-level (i.e., $m \rightarrow m + 1$) transitions of the system. This conclusion can easily be experimentally verified, since hysteresis effects, which can be observed without difficulty, are inevitably connected with such transitions. It is quite probable that such hysteresis effects have already been observed, but have not been correctly interpreted. Thus, Pegrum and Guenault⁶ relate the experimentally observed strong thermoelectric effect and the accompanying hysteresis phenomena to the remanent external field frozen in the field and its effect on the penetration depth. From the standpoint of the above-developed theory the frozen-in flux is not "spurious," but arises spontaneously. In Ref. 5. Zavaritskii, who observed low h_1 values in his experiment, gives special attention to the m = 0state, and takes pains to ensure the reversibility of the effect under temperature-gradient inversion. Possible irreversibility manifestations are rejected as being due to insufficiently pure experimental conditions.⁵⁾ In view of the foregoing, special experimental investigations of the hysteresis effects in a thermoelectric ring with the object of verifying the predictions made above are desirable. Such experiments are made even more desirable by the fact that they can provide valuable information about the role of the fluctuation effects and about the height of the fluctuation barrier separating levels with different m.

An interesting prediction of the theory developed above is the conclusion that, when the thermoelectric ring is heated, the transition into the normal state (i.e., the complete penetration of the field) should occur not at $T = T_c$, but at some temperature $T_c^* < T_c$. The experimental data reported in Ref. 8 do not contradict this conclusion.

The formulas obtained in the present paper also indicate a strong dependence of the effect under discussion on the dimensions and geometry of the system and on the presence of impurities and weak spots in the ring. The level-tolevel transitions should clearly be accompanied by nonstationary processes (in particular, by the emission of electromagnetic waves).⁶ It is also clear that the action of an external variable electromagnetic field should facilitate the $m \rightarrow m + 1$ transitions. Furthermore, the transition to the normal state should be accompanied by the appearance of a longitudinal electric field in the metal and other nonequilibrium effects.^{1,32} Therefore, further comprehensive experimental investigations of both the thermoelectric system and the related case of a hollow cylinder in an external field in the vicinity of the critical temperature T_c are desirable.

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- ¹⁾We do not consider here the longitudinal electric field arising from the interconversion of the normal and superconducting currents at the soldered joints (for greater details, see Ref. 1).
- ²⁾We consider this hypothesis (see Refs. 6 and 11) to be inadmissible, since the explanation of the experimentally observed effect requires the existence of too high a field in the surface layer.
- ³⁾The expression (2.6) assumes a symmetrical form if we formally introduce integration over the parameter d A':

$$\Phi_{s} = F_{s0} + \int_{V} \left\{ \frac{B^{2}}{8\pi} - \frac{1}{c} \int_{0}^{s} \mathbf{j}_{s}(\mathbf{A}') d\mathbf{A}' - \frac{1}{c} \int_{0}^{s} \mathbf{j}_{n} d\mathbf{A}' \right\} dv.$$
(2.6')

Here $j_s(A)$ is given by the formula (2.5); the quantity dA' has the meaning of an arbitrary variation, and does not, generally speaking, satisfy the Maxwell equations.

- ⁴⁾Formulas of the type (3.12) and (3.13) were obtained by us earlier¹⁷ for the case of a thin-walled cylinder. The formulas given here are valid for arbitrary values of r_1 and r_2 . Let us draw attention to the presence in (3.12) of the parabolic $\tilde{q}h_0^2$ term, which plays an important role, and leads to the suppression of the superconductivity in high fields. This term is missed in a number of papers (see the bibliography in Ref. 17).
- ⁵¹Let us also note that Zavaritskii's experiment⁵ was performed on a sample with a significantly different geometry (a thin toroidal ring, and not a cylinder, as in the experiment of van Harlingen *et al.*⁸). Apparently, this factor leads to additional weakening of the effect under the conditions of Zavaritskii's experiment.⁵

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