Thermoelectric effects in superconductors

V. L. Ginzburg and G. F. Zharkov

P. N. Lebedev Physics Institute of the Academy of Sciences of the USSR
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Thermoelectric effects in superconductors began to be studied about 50 years ago, but until recently the opinion was widespread that they completely vanish in the superconducting state. Yet as far back as 1944 attention was called to the fact that distinctive thermoelectric effects should arise within the framework of the two-fluid concept (allowing for the possible existence in a superconductor of a normal current as well as a superconducting current). Concretely, in an isotropic but inhomogeneous superconductor, or else in a homogeneous but anisotropic one, a thermocurrent and a magnetic field associated with it should arise in the presence of a temperature gradient. Generally these effects are small, yet in recent years they have become accessible to measurement, and a number of pertinent experimental studies have appeared. On the other hand, progress has also been made in the field of theory, in particular, in understanding the nature and various features of thermoelectric phenomena in superconductors. This article is devoted to a general physical and more detailed theoretical analysis of the problem of thermoelectric effects in superconductors. The content of the article in greater detail is evident from the table of contents.

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INTRODUCTION

Thermoelectric effects in superconductors began to be studied as early as 50 years ago (see Ref. 1 and the literature cited there). In the first stage it was concluded that "all thermoelectric effects vanish completely in the superconducting state",[1] and this conclusion remained widely held until recently.[2-6] We shall explain what the problem was using the example of measuring the thermo-emf (the Seebeck effect). If one has a circuit of two different metals existing in the normal state, with the junctions 1 and 2 being at different temperatures T_1 and T_2, then a thermo-emf $\mathscr{E}$ arises in the open circuit (Fig. 1a). In the same circuit when closed (Fig. 1*b*, a certain current $I=\mathscr{E}/R$ flows. Here R is the resistance of the circuit. However, let both metals in the circuit under consideration be superconductors cooled below their critical temperatures T_{cI} and T_{cII}. (That is, the two temperatures T_1 and T_2 are both below the lower of the temperatures T_{cI} and T_{cII}, and thus the entire circuit is superconducting.) Heretofore no one has succeeded under these conditions in detecting an emf in the open circuit nor a current in the closed circuit.[1] In any case, the effect is many orders of magnitude weaker than in a normal circuit. Moreover, if we treat a superconductor as a conductor having zero resistance, then in the presence of an emf, the current in it should grow and hence become considerable after a certain time. Yet, to a high degree of accuracy, experiment shows that no such growth of current is observed.[1,7] This circumstance has also been interpreted as proving the absence of a thermo-emf in superconductors. This conclusion agrees also with the behavior of a mixed circuit containing a normal (nonsuperconducting) part; in such a circuit (Fig. 2) the current or the emf (for an open circuit) is determined by the normal part, as if the superconducting (unshaded) part of the circuit contributed nothing to the current nor to the emf. Experiments have also given no indication of the appearance in a superconducting circuit of a Peltier heat nor of a nonzero Thomson coefficient.[1]

Nevertheless, thermoelectric effects by no means vanish in superconductors, and in principle they can be observed. This fact was noted more than 30 years ago[8,9] on the basis of the two-fluid model of superconductors, according to which the total current density in a superconductor $\mathbf{j}=\mathbf{j}_s+\mathbf{j}_n$ is the sum of two quantities. Here $\mathbf{j}_s$ and $\mathbf{j}_n$ are respectively the superconducting and the normal current densities. In the presence of a temperature gradient ∇T, the normal current generally differs from zero, but can be compensated by the

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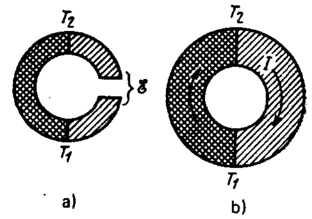

FIG. 1. Thermoelectric circuit made of normal metals. a) Open circuit ($\mathcal{E}$—thermo-emf); b) closed circuit (I—thermocurrent).

superconducting current. However, complete compensation (so that the total current $\mathbf{j}=0$) occurs only in the simplest situation, e.g., in a homogeneous and isotropic superconductor. Yet in the case of an isotropic but inhomogeneous superconductor, e.g., for a bimetallic plate (Fig. 3a), a nonzero resultant (total) current I and a corresponding magnetic field H_T arise near the junction. However, Refs. 8 and 9 paid major attention not to the case of an inhomogeneous superconductor, but to a homogeneous but anisotropic superconductor (of course we refer to homogeneity apart from the effect of the temperature gradient). In this case, when ∇T and the symmetry axes of the crystal do not coincide, a resultant current should also arise with a corresponding magnetic flux Φ_T. This effect is extremely small (specifically, the magnetic field intensity H_T that arises is small), though perhaps it has already been observed (see Sec. 4). At the same time, the conditions for observing a thermoelectric current have proved more favorable in isotropic inhomogeneous superconductors, especially if one employs a bimetallic superconducting ring (Fig. 3b) or the topologically equivalent but practically more convenient superconducting circuit made of two different metals (Fig. 4). The possibility of observing the effects in a ring (circuit) was noted only in 1973 in Ref. 10 (see also Ref. 11), but in them the concept was employed of the appearance of a phase difference of the wave function in an inhomogeneous superconductor in the presence of a temperature gradient. Hence it was thought[10] that the effect discussed there differed completely from the effect described in Refs. 8 and 9, where the treatment was based on the London theory without any introduction of the phase of the wave function, nor even of this function itself. Yet Refs. 8 and 10 in fact deal with exactly the same effect, as has been stressed in Ref. 12. At present we can consider the appearance of a current (and of the corresponding magnetic flux) in a completely superconducting circuit (consisting, of course, of different superconductors and in the presence of a temperature difference) to have been established experimentally.[13-15] Yet substantial uncertainties still exist here, and we cannot even consider it proven that precisely the effect discussed here

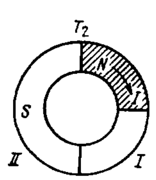

FIG. 2. Mixed circuit; the thermocurrent I is determined by the normal region N (hatched).

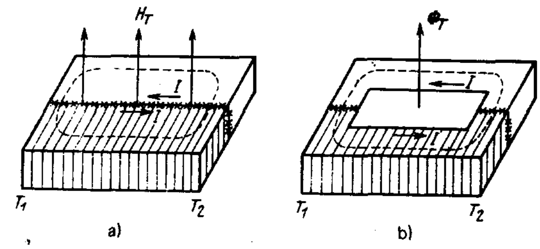

FIG. 3. a) Bimetallic superconducting plate (the field H_T arises in the region of the junction); b) bimetallic superconducting ring (the magnetic flux Φ_T arises in the aperture; $\Phi_T = H_T S$, where S is the area of the aperture).

has been isolated from the background of possible "parasitic" phenomena.[16]

In addition to those cited, an entire series of other papers (references given below) is also devoted to thermoelectric phenomena in superconductors. Our view is that this field of studies is potentially highly interesting and will be developed. At the same time, the literature contains contradictory opinions on thermoelectric phenomena in superconductors, not to speak of the lack of even a single review. Hence we hope that the publication of this review will prove justified. Below, in Chap. I we present a simple phenomenological theory of thermoelectric effects in superconductors based on the two-fluid model and the London equations. The treatment in Chap. II involves the complex order parameter Ψ. In both cases we pay special attention to methodological problems. Such an approach seems justified in view of the history and the current state of the problem. In particular, we can suppose that the insufficient attention to the experimental study of the pertinent effects is due not only to their smallness, but also to an insufficient understanding of the physical nature of thermoelectric phenomena in superconductors and of their potential importance for studying superconductivity. We shall turn to the latter problem again at the end of the article (see the concluding remarks).

I. SIMPLE PHENOMENOLOGICAL THEORY (THE TWO-FLUID MODEL, LONDON EQUATIONS)

The present state of the theory of superconductivity is such that thermoelectric effects, just like most other phenomena in superconductors, can be treated on the "highest level", on the basis of a highly refined microtheory. Yet we are convinced that we should preface such a treatment with a phenomenological description, and moreover, should begin with as simple a system as

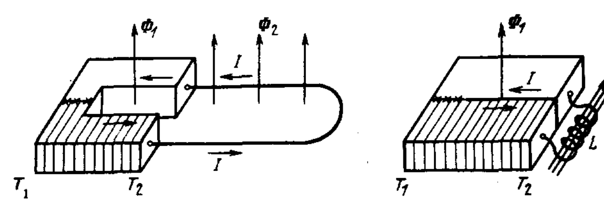

FIG. 4. Examples of a completely superconducting thermoelectric circuit. a) Plane geometry, $\Phi_T = \Phi_1 + \Phi_2$; b) circuit containing a solenoid L, $\Phi_T = \Phi_1 + \Phi_L$. The heavy line indicates a narrow gap between the superconductors.

possible. The problem of the microtheory then consists both in substantiating such a system and defining its limits of applicability, and in calculating (or estimating) the kinetic and other coefficients that enter into the equations. Starting with the foregoing, we shall begin with a phenomenological approach, and with the simplest one that could be used and actually was applied to the problems of interest to us[8,9] prior to the creation of the modern theory of superconductivity. Concretely, we have in mind the two-fluid model and the London theory, on which we shall base our treatment in this section.

1. Initial relationships

The theoretical scheme that we have just mentioned as applied to homogeneous superconductors in the absence of a temperature gradient reduces to the following system of equations for the current densities $\mathbf{j}_s$ and $\mathbf{j}_n$ (see, e.g., Refs. 9 and 17):

$$\mathrm{curl}\,\Lambda\mathbf{j}_s = -\frac{1}{c}\mathbf{H}, \tag{1.1}$$

$$\frac{\partial\Lambda\mathbf{j}_s}{\partial t} = \mathbf{E}, \tag{1.2}$$

$$\mathbf{j}_n = \sigma_n\mathbf{E}. \tag{1.3}$$

Here Λ is a coefficient that depends on the temperature, while σ_n is the conductivity of the "normal" electrons in the superconductor, which of course also depends on the temperature. In an isotropic metal or in crystals of cubic symmetry, Λ and σ_n are scalars, while in crystals of lower symmetry we must introduce in place of Λ and σ_n the corresponding second-order tensors (see Sec. 4). When not expressly stipulated, we shall assume below for brevity that the metal is isotropic (apart from Sec. 4, which is concerned with the anisotropic case).

We note that the system of equations (1.1)–(1.3) also holds for alternating fields; hence we must supplement it with the complete system of electrodynamic equations:

$$\mathrm{curl}\,\mathbf{H} = \frac{4\pi}{c}\mathbf{j} + \frac{1}{c}\frac{\partial\mathbf{E}}{\partial t}, \quad \mathrm{curl}\,\mathbf{E} = -\frac{1}{c}\frac{\partial\mathbf{H}}{\partial t}, \tag{1.4}$$

$$\mathrm{div}\,\mathbf{H} = 0, \quad \mathrm{div}\,\mathbf{E} = 4\pi\rho. \tag{1.5}$$

Equations (1.4) and (1.5) give rise to the continuity equation

$$\frac{\partial\rho}{\partial t} + \mathrm{div}\,\mathbf{j} = 0, \tag{1.6}$$

and moreover we have for superconductors

$$\mathbf{j} = \mathbf{j}_s + \mathbf{j}_n. \tag{1.7}$$

Above, $\mathbf{E}$ and $\mathbf{H}$ are the electric and magnetic field intensities (we do *not distinguish* the magnetic field $\mathbf{H}$ from the induction $\mathbf{B}$, which actually figures in all the equations; moreover we assume in Eq. (1.4) that the component of the dielectric constant that is not associated with the current $\mathbf{j}$ is unity). Here the expressions (1.1)–(1.3) play the role of "material equations", as they are sometimes called. Of course, here the densities $\mathbf{j}_s$ and $\mathbf{j}_n$ have a macroscopic meaning (in the case of $\mathbf{j}_n$ this involves statistical averaging by using the corresponding distribution function for the "normal" electrons). Below we shall be mainly interested in the steady-state case or in processes of sufficiently low frequencies that we can neglect the displacement current $\partial\mathbf{E}/\partial t$ in Eq. (1.4).

It is useful to recall the very simple meaning that the London equations (1.1) and (1.2) have from the hydrodynamic standpoint. Actually, the equation of motion of an ideal charged fluid of mass density ρ_m and charge density ρ_e has the form

$$\rho_m\frac{d\mathbf{v}_s}{dt} = \rho_m\frac{\partial\mathbf{v}_s}{\partial t} + \rho_m(\mathbf{v}_s\nabla)\mathbf{v}_s = \rho_e\mathbf{E} + \frac{\rho_e}{c}[\mathbf{v}_s\times\mathbf{H}], \tag{1.8}$$

where $\mathbf{v}_s$ is the velocity of the fluid.

Taking into account the identity

$$(\mathbf{v}_s\nabla)\mathbf{v}_s = \frac{1}{2}\nabla v_s^2 - \mathbf{v}_s\times\mathrm{curl}\,\mathbf{v}_s,$$

we see that the condition (as generalized to the case of presence of a magnetic field) for possible superfluid movement has the form

$$\mathrm{curl}\,\mathbf{v}_s = -\frac{\rho_e}{\rho_m c}\mathbf{H}. \tag{1.9}$$

If we introduce the superconducting current density $\mathbf{j}_s = \rho_e\mathbf{v}_s$ and assume the quantities ρ_e and ρ_m to be independent of the coordinates, then the condition (1.9) transforms into the fundamental London equation (1.1), with

$$\Lambda = \frac{\rho_m}{\rho_e^2} = \frac{m}{e^2 n_s} = \frac{m^*}{e^{*2}n_s^*}. \tag{1.10}$$

Here we have set $\rho_m = mn_s = m^*n_s^*$ and $\rho_e = en_s = e^*n_s^*$ and have used the notation $e^* = 2e, m^* = 2m$, in line with the notion of bound Cooper pairs; $n_s^* = n_s/2$ is the pair density; n_s is the density of "superconductive" electrons (e is the charge of an electron, and m is its mass). Thus we can treat the charged superconducting fluid as consisting of particles of mass $m^* = 2m$ and charge $e^* = 2e$.

Under the condition (1.9), Eq. (1.8) acquires the form

$$\frac{\partial\Lambda\mathbf{j}_s}{\partial t} = \mathbf{E} - \nabla\frac{\Lambda j_s^2}{2\rho_e}, \quad \mathbf{j}_s = en_s\mathbf{v}_s = e^*n_s^*\mathbf{v}_s, \tag{1.11}$$

i.e., it transforms into (1.2), if we neglect the last term on the right-hand side of (1.8). Generally this term is small and one usually can actually neglect it. Yet it arises in a quite natural manner, has been introduced in the past (see, e.g., Refs. 9 and 17), and has recently attracted interest anew (effects involving this term are discussed in greater detail in Sec. 9).

Above, we stipulated that the superconductor is taken to be homogeneous. Also we did not allow for the possible existence of a temperature gradient or the presence of other nonequilibrium situations. Let us pose the problem of what will happen if we reject these assumptions.

It is evident by analogy with ordinary hydrodynamics that a term of the type $-\nabla p_s$ can arise on the right-hand side of Eq. (1.8), where p_s is a certain pressure. A more detailed analysis of the equations of two-fluid hydrodynamics indicates that the additional term in question has the form $-\rho_m\nabla\mu$, where μ is the chemical potential of the electrons. Bearing in mind applications to nonequilibrium situations in which one must distinguish the chemical potentials of the superconductive and normal electronic subsystems, let us denote the chemical potential introduced above by μ_{s0}, and therefore write the corresponding generalization of Eq. (1.11) in the form

$$\frac{\partial \Lambda \mathbf{j}_s}{\partial t}=\mathbf{E}-\frac{\nabla\mu_s}{e}. \tag{1.12}$$

Here we have

$$\frac{\nabla\mu_s}{e}=\frac{\nabla\mu_{s0}}{e}+\nabla\frac{\Lambda j_s^2}{2\rho_e}.$$

Taking into account the fact that $\mathbf{j}_s=en_s\mathbf{v}_s$ and $\Lambda=m/e^2n_s$ [see (1.10)], Eq. (1.12) is evidently equivalent to:

$$m\frac{\partial \mathbf{v}_s}{\partial t}=e\mathbf{E}-\nabla\mu_s, \tag{1.13}$$

where we have

$$\nabla\mu_s=\nabla\mu_{s0}+\nabla\frac{mv_s^2}{2}. \tag{1.14}$$

However, we must remember that the two-fluid model implies the conclusion[6,18-20] that the quantity μ_{s0} itself depends on v_s^2. Thus taking terms of the order of v_s^2 into account requires a special treatment (see Sec. 9; we shall neglect the role of terms of the order of v_s^2 in the rest of the sections).

Moreover we note that the equation

$$\frac{\partial \Lambda \mathbf{j}_s}{\partial t}=\mathbf{E}-\nabla\xi,$$

where ξ is an arbitrary scalar (and therefore, in particular, Eq. (1.12) as well), leads to the following relationship in view of the field equation curl $\mathbf{E}=-c^{-1}\partial\mathbf{H}/\partial t$:

$$\frac{\partial}{\partial t}\left(\operatorname{curl}\Lambda\mathbf{j}_s+(1/c)\,\mathbf{H}\right)=0.$$

This latter expression is, of course, compatible with (1.1). Thus, in any case Eqs. (1.1) and (1.12) do not contradict one another.

For a metal in the normal state, we can account for nonequilibrium in a certain approximation by replacing Ohm's law $\mathbf{j}=\sigma\mathbf{E}$ by the more general expression[1)]

$$\mathbf{j}=\sigma\left(\mathbf{E}-\frac{\nabla\mu}{e}\right)+b\nabla T. \tag{1.15}$$

Here μ is the chemical potential of the electrons in the metal. In the case of a superconductor, it is therefore natural to employ an expression similar to (1.15) for the normal current $\mathbf{j}_n$. That is, instead of (1.3) we write

$$\mathbf{j}_n=\sigma_n\left(\mathbf{E}-\frac{\nabla\mu_n}{e}\right)+b_n\nabla T. \tag{1.16}$$

Here σ_n, μ_n, and b_n depend on the temperature, and also generally on the coordinates (for an inhomogeneous superconductor).[2)] It may prove convenient to use also the doubled chemical potential of the normal electrons $\mu_n^*=2\mu_n$, which generally differs from $\mu_s^*=2\mu_s$. (The meaning of the quantities μ_s^* and μ_n^* is clarified in Sec. 5).

In the steady-state case (i.e., when $\partial\mathbf{v}_s/\partial t=0$), Eq. (1.13) implies that

$$e\mathbf{E}=\nabla\mu_s.$$

Then we get from (1.16) the following expression for the normal current density:

$$\mathbf{j}_n=\sigma_n\nabla\frac{\mu_s-\mu_n}{e}+b_n\nabla T. \tag{1.17}$$

If we neglect terms of the order of v_s^2 and the possible difference between μ_s and μ_n by assuming that $\mu_s=\mu_n=\mu$ (as has been done in Refs. 8, 9, and 17), then the equation for $\mathbf{j}_s$ (1.12) is written in the form

$$\frac{\partial \Lambda \mathbf{j}_s}{\partial t}=\mathbf{E}-\frac{\nabla\mu}{e}, \tag{1.18}$$

while the expression for $\mathbf{j}_n$ acquires the especially simple form

$$\mathbf{j}_n=b\nabla T. \tag{1.19}$$

Later on in Section I we shall treat the steady-state conditions and base our discussion on Eqs. (1.18) and (1.19) and Eq. (1.1) or their generalizations to the anisotropic case (subsection 4). The effects associated with the appearance of a difference between the chemical potentials $\delta\mu=\mu_s-\mu_n$ and also those involving terms of the type $mv_s^2/2$ will be treated in Sec. 9.

2. Isotropic superconductors and superconducting circuit

Current cannot flow in the normal state in an open conductor, and according to (1.15), the following electric field arises:

$$\mathbf{E}=\nabla\frac{\mu}{e}-\frac{b}{\sigma}\nabla T. \tag{2.1}$$

Concretely, Fig. 5a illustrates the situation in a rectilinear specimen (q is the charge density, which is concentrated at the ends of the specimen).

As is evident from (1.19), a normal current $\mathbf{j}_n$ arises in a superconductor in the presence of a temperature gradient. Here this fact does not contradict the absence of a total current $\mathbf{j}=\mathbf{j}_s+\mathbf{j}_n$, since the current $\mathbf{j}_n$ can be fully compensated by the current $\mathbf{j}_s$ (Fig. 5b). With such a compensation, according to (1.18) and (1.19) we have

$$\mathbf{j}=\mathbf{j}_s+\mathbf{j}_n=0,\quad \mathbf{E}-\frac{\nabla\mu}{e}=0,\quad \mathbf{j}_n=b_n\nabla T. \tag{2.2}$$

Under conditions corresponding to Fig. 5b, precisely this total compensation of currents occurs, whereby the charge $q=0$. Of course, here the magnetic field $\mathbf{H}$ is also zero, and Eq. (1.1) is satisfied. Actually, according to (2.2) we have

$$\begin{aligned}\operatorname{curl}\Lambda\mathbf{j}_s &= -\operatorname{curl}\{\Lambda(T)\,b_n(T)\,\nabla T\}\\ &= -\Lambda b_n\operatorname{curl}\nabla T-[\nabla\{\Lambda(T)\,b_n(T)\},\,\Delta T]=0.\end{aligned}$$

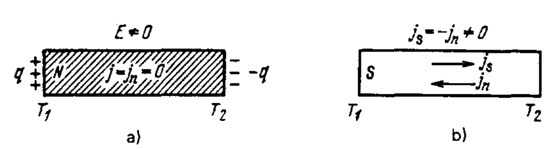

FIG. 5. Inhomogeneously heated metals. a) Normal metal; the charges $\pm q$ arise; b) superconductor; the countercurrents $\mathbf{j}_s=-\mathbf{j}_n$ arise.

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1) The flux of electrons is directed opposite to ∇T, i.e., in the direction of decreasing temperatures, while the current flows in the opposite direction. Thus the coefficient b and the coefficient b_n used below are both positive.

2) We note that, since a superconducting current does not transport heat, there are no grounds for introducing a term of the type $b'\nabla T$ into the right-hand side of (1.12) (additional arguments in support of this are found in Ref. 8; see also Refs. 4–6).

The opposing normal and superconductive currents that arise in an open specimen (or circuit) are quite analogous to the fluxes of normal and superfluid liquid that arise in the presence of a temperature difference in helium II (see, e.g., Refs. 6, 9, 18–20). At one time the analogy with superfluid helium led one of the authors to the idea[8,9] of the possible existence of thermoelectric effects in superconductors.

Whenever the total current is zero [see (2.2)], the existence of the current $\mathbf{j}_n$ affects only the heat transport. However, the corresponding effect (convective heat transport), which leads to an extra contribution to the effective heat conductivity characterized by the coefficient $\varkappa_c$, is very small.[21-23 3)]

Yet if a superconductor, though isotropic, is inhomogeneous, i.e., the coefficients Λ and b_n respectively in (1.1) and (1.18)–(1.19) depend on the coordinates (in addition to the variation caused by the temperature gradient), then the solution (2.2) is generally no longer valid. In other words, a resultant current and its corresponding magnetic field can arise. As we remarked in the Introduction, such a case has been discussed in Refs. 8 and 9 with the example of a bimetallic plate (Fig. 3a). One must solve this problem on the basis of Eqs. (1.1), (1.4), and (1.19). Yet in Ref. 8 only an estimate was made of the field H_T that arises, since the case of a bimetallic plate was deemed "dirty", and thereby less interesting than the inhomogeneously heated anisotropic superconductor (see subsection 4). If we consider a continuous bimetallic plate, then this configuration seems actually of little interest. However, one can make an aperture in the plate (Fig. 3b) and also transform it into a topologically equivalent circuit that corresponds to an ordinary thermoelectric circuit (see Fig. 4). The main thing of interest in this circuit is not the current and field distribution, but the total current I or the magnetic flux through the circuit. But we can find this flux Φ_T by a simple method that has been widely used also in other cases (e.g., in proving the quantization of the magnetic flux trapped by a superconductor; see Subsection 8).

Let us take up this problem in somewhat greater detail. Evidently, we can write the solution of Eq. (1.1) in the form

$$\Lambda \mathbf{j}_s = -\frac{1}{c}\mathbf{A} + \nabla\zeta, \tag{2.3}$$

where $\mathbf{A}$ is the vector potential (curl $\mathbf{A} = \mathbf{H}$), and ζ is some scalar.

Staying within the framework of the ideas of classical field theory, we can naturally consider the scalar ζ (and also the vector potential $\mathbf{A}$) to be a single-valued function of the coordinates. Then, upon integrating over any closed contour we shall have

$$\oint \nabla\zeta \cdot d\mathbf{l} = 0. \tag{2.4}$$

Evidently under this condition we will not be able to describe the well-known vortex filaments in superconductors or in a superfluid liquid since the condition (2.4) is not satisfied on passing around a filament. In order to include vortices in superconductors in the discussion, we must either replace (2.4) by the following more general expression arising from a quantization condition (such as the Bohr condition):[4)]

$$\oint \nabla\zeta \cdot d\mathbf{l} = n\frac{h}{e^*} = n\frac{h}{2e}, \qquad n = 0, 1, 2, \ldots \tag{2.5}$$

($h = 2\pi\hbar$ is Planck's constant), or we must go over from the London scheme to a more general description of superconductivity that employs the concept of a complex order parameter (the macroscopic wave function Ψ). In the latter case the condition (2.5) is derived from requiring the wave function to be single-valued and from studying its phase. Since Bohr's quantization condition is grounded precisely in the requirement that the wave function should be single-valued, we are dealing here essentially with the same derivation of Eq. (2.5). It will be used in Subsections 5 and 6, while here we shall take as our basis Eq. (2.4) and analyze some consequences that stem from the London equations without taking vortices into account.

In the steady-state case we get the following equation from Eqs. (1.1), (1.4), and (1.5) with $\mathbf{j}_n = 0$:

$$\Delta\mathbf{H} - \frac{1}{\delta^2}\mathbf{H} = 0, \tag{2.6}$$

$$\delta^2 = \frac{\Lambda c^2}{4\pi} = \frac{mc^2}{4\pi e^2 n_s} = \frac{m^* c^2}{4\pi e^{*2} n_s^*}. \tag{2.7}$$

In particular, it has the solution $H = H_0 e^{-x/\delta}$, where $\delta \equiv \delta_L$ is the London penetration depth of the magnetic field into the superconductor. In the absence of a temperature gradient, we have precisely $\mathbf{j}_n = 0$, and hence also $\mathbf{j}_s = 0$ in the interior of the superconductor (in particular, for a superconducting circuit that consists of a material of thickness $d \gg \delta$). Hence, upon integrating (2.3) over a contour lying in the interior of the material

3)Generally the major role in convective heat transport is played by the breakdown of superconductive pairs as the current $\mathbf{j}_n$ arises at the temperature T_2 and by the production of pairs from normal electrons (excitations) at the temperature $T_1 < T_2$, at which the current $\mathbf{j}_n$ is converted into the current $-\mathbf{j}_s$. This process is associated with the heat flux $\mathbf{W} \sim \mathbf{j}_n\Delta/e = b_n\Delta(T)\nabla T/e$, where 2Δ is the energy per pair (the charge $e^* = 2e$). Hence it is evident that $\varkappa_c \lesssim b_n\Delta(0)/e \sim b_n k T_c/e$, whereas the ordinary electronic thermal conductivity is $\varkappa_e \sim (\pi^2k^2/3e^2)\sigma_n T$. Moreover, the differential thermo-emf is $d\mathscr{E}/dT \equiv \alpha = b/\sigma \sim 3\times10^{-11}$ CGSE/°K $\sim 10^{-8}$ V/°K (see subsection 3; we give here the value for pure tin near T_c; the earlier uncertainty concerning temperature dependence of $d\mathscr{E}/dT$ for $T \geq T_c$ has been eliminated in Ref. 24). In view of the foregoing, we get the estimate $(\varkappa_c/\varkappa_e)_{T\sim T_c} < 10^{-6}(d\mathscr{E}/dT)_{T_c} \sim 3\times10^{-6}$.

4)Here we conduct the discussion as follows. In the case of superfluidity, we have $\mathbf{v}_s = \nabla\zeta$, and Bohr's quantization condition gives $\oint m^*\mathbf{v}_s \cdot d\mathbf{l} = nh$, whence we get $\oint \nabla\zeta \cdot d\mathbf{l} = nh/m^*$ is the mass of the corresponding particle (e.g., a helium atom). According to (1.10) and (2.3), a superconductor has $m^*\mathbf{v}_s/e^* = -(\mathbf{A}/c) + \nabla\zeta$, and the condition of quantization

$$\oint \mathbf{P}_s \cdot d\mathbf{l} = \oint \left(m^*\mathbf{v}_s + \frac{e^*}{c}\mathbf{A}\right)\cdot d\mathbf{l} = e^*\oint \nabla\zeta d\mathbf{l} = nh$$

leads to (2.5).

and taking into account the fact that

$$\oint \mathbf{A}\cdot d\mathbf{l} = \int \operatorname{curl}\mathbf{A}\cdot d\mathbf{S} = \int \mathbf{H}\cdot d\mathbf{S} = \Phi,$$

we see that, in the absence of vortices or of a "frozen-in" flux [see (2.4)], the magnetic flux through the contour under consideration is

$$\Phi = 0. \tag{2.8}$$

In an inhomogeneously heated superconductor we now have $\mathbf{j}_n \neq 0$ and $\mathbf{j}_s \neq 0$ in the interior of the metal, and at least in a region of homogeneity, $\mathbf{j}_s = -\mathbf{j}_n = -b_n \nabla T$ [see (2.2)]. Hence, except for the region of the junctions, we have the following relationship everywhere on the contour indicated by the dotted line in Fig. 3 [see (2.3) and (2.7)]:

$$-c\Lambda \mathbf{j}_s = c\Lambda b_n \nabla T = \frac{4\pi}{c} b_n(T)\,\delta^2(T)\,\nabla T = -\mathbf{A} - c\nabla\zeta. \tag{2.9}$$

Integrating (2.9) over the stated contour and taking (2.4) into account, we obtain the flux of the magnetic field through this contour:

$$\Phi = \Phi_T = \frac{4\pi}{c}\int_{T_1}^{T_2} [b_{n\mathrm{I}}(T)\,\delta_\mathrm{I}^2(T) - b_{n\mathrm{II}}(T)\,\delta_\mathrm{II}^2(T)]\,dT. \tag{2.10}$$

Here the subscripts I and II refer to the different metals I and II.

Thus, in an inhomogeneously heated circuit made of different kinds of superconductors, i.e., when $b_{n\mathrm{I}}(T)\delta_\mathrm{I}^2(T) \neq b_{n\mathrm{II}}(T)\delta_\mathrm{II}^2(T)$, a certain superconducting current flows of magnitude $I = c\Phi_T/L_s$, where Φ_T is the flux (2.10) and L_s is the self-induction coefficient of the superconducting ring.

Of course, the current I flows over the inner surface of the ring in a layer of thickness of the order of δ near the surface of the superconductor. Indeed, we have neglected thus far the region of the junctions (double cross-hatching in Fig. 3b). Yet evidently the effect of (2.10) is an integral one, and for a sufficiently large contour the role of the junctions can be made arbitrarily small.

Although the effect under consideration has perhaps already been observed (see subsection 3) yet it is very small in comparison with the thermocurrent in a normal metal. In fact, for the sake of simplicity let us study a circuit that consists of a circle of radius r formed of a nonsuperconducting wire having different values of b, but everywhere having the same conductivity σ and cross-section $S = \pi\rho^2$. The current in this circuit is

$$I_n = \frac{\mathscr{E}_n}{R_n} \sim \frac{\rho^2}{r}\oint b\,dT, \quad \mathscr{E}_n = \oint \frac{b}{\sigma}\,dT, \quad R_n = \frac{2\pi r}{\sigma S} = \frac{2r}{\sigma\rho^2},$$
$$\Phi_n \sim \pi r^2 H \sim \frac{\pi I_n r}{c}.$$

But if a circuit having the same values of r, ρ, and b and constant penetration depth δ is completely superconducting, then according to (2.10) we have

$$\Phi_T \sim \pi r^2 H \sim \frac{4\pi}{c}\delta^2 \oint b\,dT, \quad H \sim \frac{1}{c}\frac{I}{r}, \quad I \sim \frac{\delta^2}{r}\oint b\,dT. \tag{2.12}$$

Thus in the case under consideration we have

$$\frac{\Phi_T}{\Phi_n} \sim \frac{I}{I_n} \sim \left(\frac{\delta}{\rho}\right)^2. \tag{2.13}$$

This ratio is usually very small (e.g., for wires of radius $\rho \sim 0.1$ cm and for $\delta \sim 10^{-5}$ cm, the ratio (2.13) is of the order of 10^{-8}).

It is highly important to understand what happens upon breakdown of the condition $(\delta/\rho)^2 \ll 1$, upon which we have relied above. If we do not take into account the action of the magnetic field that is created by the thermoelectric current itself (this seems allowable, at least for a weak enough thermocurrent), the transition from the superconducting to the normal state is a second-order transition. Hence we should expect upon an appropriate temperature increase a continuous transition from a pure superconducting circuit to a partially normal circuit (Fig. 2). Concretely, let us imagine a completely superconducting circuit of the type depicted in Fig. 1b, and let the temperatures T_2 and T_1 of the junctions rise (for simplicity we can conveniently assume the difference $T_2 - T_1$ to be constant). Then as the temperature T_2 reaches the value T_{cI} (the critical temperature of metal I; we assume that $T_{cII} > T_{cI}$), the transition begins to take place to a mixed (partially normal) circuit (see Fig. 2), for which the thermoelectric current is already considerable (as compared with the thermocurrent in the completely superconducting circuit). Such considerations force us to assume that when $T \to T_{cI}$, the thermoelectric current in the superconducting circuit I approaches the current I_n in the corresponding normal circuit. Yet when $T \to T_{cI}$, the depth of penetration $\delta(T \to T_{cI}) \sim \infty$, and of course, the estimate (2.13) is inapplicable (this estimate, though not explicitly, is based on the assumption that $(\delta/\rho)^2 \ll 1$).

The foregoing is confirmed upon more detailed treatment. Thus, we consider a plane, thin film of thickness d under conditions in which $(d/\delta)^2 \ll 1$. In this film we can consider in the first approximation that the current densities j, j_s, and j_n are independent of the z coordinate directed perpendicular to the film ($z = 0$ at the center of the film; of course we also assume the current densities to be independent of the coordinates x and y). In the absence of an external magnetic field, the magnetic field of the current $I = jd$ that flows through the film and is directed along the x axis is $H(z) = 8\pi c^{-1} jz$ (for $|z| \leq d/2$). Outside the film we have $H = H_0 = 4\pi I/c = 4\pi jd/c$. At the same time the total current density is[5)] $\mathbf{j} = \mathbf{j}_s + \mathbf{j}_n = -\mathbf{A}/c\Lambda + b_n \nabla T$. Here the vector potential $\mathbf{A}$ is directed along the y axis, and in magnitude is equal to $A = 4\pi c^{-1} jz^2$. Thus we have $j_s = -A/c\Lambda = -cA/4\pi\delta^2 = -z^2 j/\delta^2$, and evidently we must have $j_s \ll j$, since under the discussed conditions $z^2/\delta^2 \leq d^2/\delta^2 \ll 1$. However, this means that $j \approx j_n = b_n(T_{cI})\nabla T$, i.e., the total current approaches its value in the normal state. Thus, in the immediate vicinity of T_c (i.e., as $\delta \to \infty$), we shall have $\Phi_T/\Phi_n \sim 1$ instead of the estimate (2.13).

3. The thermocurrent in a superconducting circuit (relation to experiment)

Although the thermocurrent in a superconducting circuit is generally small in comparison with the current in a normal circuit, it is quite measurable with modern apparatus (superconducting quantum interferometers,

5)Cf. (2.2) and (2.3); we can easily see that we can set $\nabla\zeta = 0$ in (2.3).

etc.). Moreover, as we have noted, the thermocurrent in a superconducting circuit has apparently been measured experimentally[13-15] (see also Refs. 25–27). Yet the problem of comparing theory with experiment remains open. In particular, the role is uncertain of the masking effect[16] caused by the relationship of the depth of penetration δ to the temperature. Moreover, we do not know a number of the details of the experiment, and primarily, we are not competent to discuss the methodology of the measurements. All this impels us to refrain from discussing the performed experiments in any detail. We shall only give several simple expressions that bring Eq. (2.10) to a more specific form, and shall make some estimates and remarks.

The thermoelectric coefficient $b_n(T)$ in the superconducting state rapidly declines with falling temperature. Of course, this is quite understandable, since the number of "normal" electrons declines with falling T. Under the assumption that the scattering of the "normal" electrons is governed by impurities rather than by phonons (i.e., in the region of residual resistance), with the mean free path being substantially longer than the coherence length, we can use the following expression for $b_n(T)$:[6)]

$$b_n(T) = b(T_c)\cdot\frac{3}{2\pi^2}\int_x^\infty \frac{y^2\,dy}{\cosh^2(y/2)}. \qquad (3.1)$$

Here $b(\mathscr{E}_c)=\sigma\alpha$ is the coefficient in the normal state (σ is the conductivity, and $\alpha \equiv d\mathscr{E}/dT$ is the differential thermo-emf)[7)], and $x=\Delta(T)/kT$, where $\Delta(T)$ is the width of the superconducting gap. Figure 6 shows the $b_n(T)/b(T_c)$ relationship according to (3.1). We note that whenever the scattering amplitude does not depend on the momentum we have

$$b(T)=\frac{2\pi^2}{9}\frac{ek^2T}{m}\frac{d}{d\varepsilon}[\tau(\varepsilon)\,v(\varepsilon)\,\varepsilon]_{\varepsilon=\mu}=\frac{\pi^2}{9}ek^2T\frac{d}{d\mu}[\tau v v^2]_{\varepsilon=\mu}. \qquad (3.2)$$

Here we must take the absolute magnitude of the charge of the electron e (i.e., $e>0$), $\tau(\varepsilon)$ is the relaxation time, $\mu=\varepsilon_0$ is the chemical potential (energy at the Fermi surface), and in transforming to the last expression we assume the energy ε to be $\varepsilon=mv^2/2$ (see Refs. 10, 29, and 30); under the same conditions $\sigma=(1/3)e^2[\tau v v^2]_{\varepsilon=\mu}$, and hence[29,30] we have

$$\alpha=\frac{b}{\sigma}=\frac{\pi^2k^2T}{3e}\frac{d}{d\mu}[\ln(\tau v v^2)_{\varepsilon=\mu}]. \qquad (3.3)$$

For free electrons scattered by impurities, we have $\tau=l/v$, where l does not depend on $\mu, v=\sqrt{2\mu/m}$, and $\nu = m^2v/\pi^2\hbar^3$. Hence we have

$$\frac{d}{d\mu}[\ln(\tau v v^2)_{\varepsilon=\mu}]=\frac{1}{\mu},\quad \alpha=\frac{\pi^2}{3e}\frac{k^2T}{\mu}. \qquad (3.4)$$

Under the same conditions, the conductivity σ does not depend on the temperature, and $b=\sigma\alpha\sim T$. Thus, for

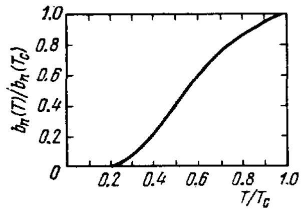

FIG. 6. Dependence of the thermoelectric coefficient b_n on the temperature T.

the normal state, the coefficient b near T_c depends weakly on T, and we can set it equal to $b(T_c)$. According to (3.4), $\alpha\sim 10^{-10}T(^\circ\mathrm{K})/\mu(\mathrm{eV})$, or for $T\sim 3^\circ$K and $\mu \sim 10$ eV, we have $\alpha=3\times10^{-11}$ CGSE/°K~10^{-8} V/°K. Acutally in tin near $T_c=3.72^\circ$K one observes[31] α attaining values as high as 5×10^{-8} V/°K upon adding a certain amount of impurities. Tin was used in Ref. 13 for which

$$b = 54\ \mathrm{V/^\circ K\cdot ohm\cdot cm} = 1.62\cdot10^{11}\ \mathrm{CGSE/^\circ K},$$

and another specimen having a value of b smaller by a factor of 27. The value of α can increase substantially in the presence of magnetic impurities (by two-three orders of magnitude). Perhaps this situation can be conveniently exploited[32] for studying thermoelectric effects in superconductors.

We stress that one must undoubtedly use the experimental value of $b(T_c)$ in analyzing thermoeffects in superconductors, rather than undertaking any calculations whatever of this quantity, which can introduce only an additional uncertainty and inaccuracy. But the coefficient $b_n(T)$ cannot be measured independently, and therefore we must resort to using Eq. (3.1); apparently we should not expect substantial errors in this method. Moreover, the temperature range of greatest interest is that directly adjoining T_c, where we can simply set $b_n(T)=b(T_c)$ in Eq. (2.10), as we shall do below.

Apart from $b_n(T)$, the formula (2.10) that is now of interest to us contains only the depth of penetration $\delta(T)$, which approaches infinity as $T\to T_c$. As we know, near T_c (when $\Delta T=T_c-T\ll T_c$) we can assume that

$$\delta^2(T)=\frac{\delta_0^2}{T_c[1-(T/T_c)]}. \qquad (3.5)$$

Sometimes the semiempirical formula $\delta^2=\delta^2(0)[1-(T/T_c)^4]^{-1}$ is also used which holds approximately throughout the temperature range; evidently here $\delta_0=\delta(0)/2$. Now let us study the case in which we have in (2.10) $b_{nI}\delta_I^2\gg b_{nII}\delta_{II}^2$, which holds near the critical temperature T_{cI} of metal I (we assume that $T_{cII}\gg T_{cI}$, or more exactly, that $T_{cII}-T_{cI}\gg T_{cII}-T$, where T is the temperature in question, which lies between T_2 and T_1). Then Eq. (2.10) takes on the form

$$\Phi=\Phi_T\approx\frac{4\pi}{c}\int_{T_1}^{T_2} b_{nI}(T)\,\delta_I^2(T)\,dT=\frac{4\pi}{c}b(T_c)\,\delta_0^2\ln\frac{T_c-T_1}{T_c-T_2}. \qquad (3.6)$$

Here the values of b, δ_0, and T_c pertain to the metal I.

Evidently, when $\Delta T=T_2-T_1\ll T_c-T_1$, we obtain from (3.6) the following linear temperature dependence instead of a logarithmic one:

$$\Phi_T=\frac{4\pi}{c}b(T_c)\,\delta_0^2\frac{\Delta T}{T_c-T_1}=\frac{4\pi}{c}b(T_c)\,\delta^2(T_1)\,\Delta T. \qquad (3.7)$$

For tin we have $\delta_0\approx 2.5\times10^{-6}$ cm and good specimens

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[6)]Cf. Refs. 10, 15, 23, and 28; here the coefficient in (3.1) has been chosen to agree with Ref. 15, whence we have also taken Fig. 6.

[7)]The thermo-emf associated with a given normal metal (in a circuit like that depicted in Fig. 2, but open) is $\mathscr{E}=\int_1^2\nabla(\varphi+\mu/e)\cdot d\mathbf{l}=\int_{T_1}^{T_2}(b/\sigma)\,dT$ [see (1.15) and (2.1)]; hence $d\mathscr{E}/dT\equiv\alpha=b/\sigma$.

show $b(T_c) \sim 10^{11}-10^{12}$. Hence, according to (3.6) we have

$$\Phi_T \sim 10^{-9} \ln \frac{T_c - T_1}{T_c - T_2} \sim 10^{-2}\Phi_0 \ln \frac{T_c - T_1}{T_c - T_2}. \quad (3.8)$$

Here $\Phi_0 = hc/2e = 2\times10^{-7}$ gauss:cm^2 is the quantum of flux.

For values $T_c - T_2 \sim 10^{-2}$ °K and $T_c - T_1 \sim 0.1$ °K, or in general, when $\ln[(T_c - T_1)/(T_c - T_2)] \sim 1$, the flux Φ_T is as much as $10^{-2}\Phi_0$, and hence, it is quite amenable to measurement. Currently, so far as we know, one can measure fluxes $\Phi \gtrsim 10^{-5}\Phi_0$ with quantum interferometers.

An experiment[13] performed with Type I superconductors (Pb and Sn) has on the whole confirmed the existence of the flux (3.6) and its temperature dependence. Here both a linear dependence (3.7) at low ΔT was found, and a more rapid increase in Φ_T as $T_2 \to T_c$ [see 3.6)]. An experiment[15] performed with hard semiconductors (Nb and Ta) traced more distinctly the logarithmic growth of Φ_T according to (3.6). However, for $\Delta T \ll 1$, the magnetic flux did not tend to zero, but took on a constant value that substantially exceeded the value obtained from the theoretical estimate (3.7). In this regard it was noted in Ref. 16 that one can obtain this result when the circuit at $T_1 = T_2$ contains a residual "frozen-in" flux (moreover, the latter is quite possible in the case of a circuit made of the hard superconductors Nb and Ta). Indeed, when we take the "frozen-in" field into account, the flux through the circuit under consideration is [see Eq. (7.7) below]:

$$\Phi = \Phi_T + n\Phi_0, \quad \Phi_0 = hc/2e = 2\cdot10^{-7}\ \text{gauss}\cdot\text{cm}^2,\ n = 0, 1, 2, \ldots$$

and at large values of n one can probably explain the anomalies observed in Ref. 15.

It was also found in the experiments of Refs. 15 and 26 that near T_c the magnitude of the thermoelectric flux in the circuit increases more rapidly than is predicted by Eq. (3.8), and immediately near T_c, the thermoelectric flux exceeds by several orders of magnitude the value estimated by Eq. (3.8). According to Ref. 16, one can understand this result if the ring contains a large "frozen-in" flux and the latter becomes redistributed in the circuit owing to local changes in the depth of penetration upon inhomogeneous heating of the superconductor.

In this regard we should recall Refs. 33 and 34, which take into account the effect of the external field on the thermoelectric effect in superconductors. It was shown[33,34] on the basis of a kinetic treatment that one should take into account terms quadratic in v_s in the expression (1.19) for the current in the presence of an external field. This causes an extra field-dependent term to appear in the coefficient b in (1.19). Under certain conditions this term can be large in comparison with the main term in (1.19), as a result of which one can observe a substantial amplification of the effect. Perhaps the anomalies observed in Refs. 15 and 26 can be explained also in the light of the remarks made at the end of subsection 2 that a continuous transition to the case of a normal metal should occur as $T \to T_c$ with a

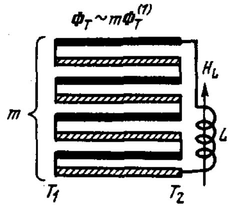

FIG. 7. Thermoelectric pile of m links. The current in the circuit is m times as large as with a single circuit.

corresponding increase in the thermoelectric flux. However, on the whole, both from the experimental and the theoretical standpoint, the problem of the temperature range close to the critical temperature remains not completely elucidated and requires further analysis.

We note in connection with the discussion of the experiments that the observed effect can be amplified considerably if one uses a thermoelectric pile[35] instead of a single thermoelectric circuit like Fig. 3 or 4. The pile amounts to a closed superconducting circuit of several links whose ends are maintained at different temperatures (Fig. 7). We can easily see that the resultant current in a circuit of m links is m times larger than in the case of a single circuit. Here one can conveniently observe not the flux Φ_T directly, but the field in an auxiliary superconducting coil L. For a given flux in the circuit, the latter can also be larger than the field in the main circuit. One can get an additional amplification of the thermoelectric current by inserting into the thermoelectric circuit (of inner radius R) a superconducting core S (Fig. 8), which crowds the field into the narrow gap (of width d) between the core and the main thermoelement. Here the flux Φ_T does not vary, while the field in the gap is increased by a factor of $R/2d$ (in proportion to the areas of the total aperture and the residual slit; we assume that $d \gg \delta$). In the case of a narrow slit, the field and the current circulating in the circuit can be enhanced by several orders of magnitude (e.g., when $R \sim 1$ cm and $d \sim 10^{-3}$ cm, we have $R/2d \sim 10^3$). Hence a circuit optimal for observation should have the smallest possible inner area (of the type of Fig. 4b).

If the aperture (slit) in the bimetallic ring is made to approach zero, while a continuous transition is made to the case of a bimetallic plate (compare Figs. 3a and b), then the field is ultimately localized in a region of the order of $\delta \sim 10^{-5}$ cm on both sides of the junction. In order of magnitude this field will amount to $H \sim 10^{-4}$ gauss, as was estimated in Refs. 8 and 9. This, in particular,

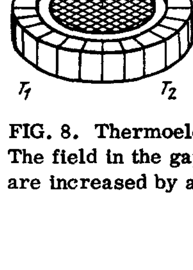

FIG. 8. Thermoelectric circuit with a superconducting core. The field in the gap and the current flowing around the circuit are increased by a factor of $R/2d$.

also makes evident the physical equivalence of the thermoelectric effect in a bimetallic plate[8,9] and in a bimetallic ring.[10]

4. Anisotropic superconductors

A thermoelectric effect (the circulation current and the corresponding magnetic field) should arise not only in an inhomogeneous superconductor, but also in a homogeneous but anisotropic superconductor. Indeed, the current differs from zero only when the temperature gradient does not coincide with the symmetry axes of the crystal. This effect was treated in Refs. 8 and 9 on the basis of the London theory generalized to the anisotropic case. The latter is achieved, as was mentioned in subsection 1, if we take the parameter Λ to be the second-order tensor Λ_{ij}. Here, since the superconducting current does not decay, $\Lambda_{ij}=\Lambda_{ji}$. To abbreviate the notation, let us introduce here the symbol $(\hat{\Lambda}\mathbf{j}_s)_i=\Lambda_{ij}j_{sj}$. Then Eq. (1.1) is written in the form

$$\operatorname{curl}\hat{\Lambda}\mathbf{j}_s=-\frac{1}{c}\mathbf{H}. \tag{4.1}$$

For isotropic superconductors or for crystals of cubic symmetry, $\Lambda_{ij}=\Lambda\delta_{ij}$, and (4.1) reduces to (1.1). In the approximation used in subsection 2, in which $\mu_s=\mu_n=\mu$, we have the following result in the anisotropic case instead of (1.9):

$$j_{n,i}=b_{n,ij}\frac{\partial T}{\partial x_j}. \tag{4.2}$$

We can write the solution of Eq. (4.1) in the form $\hat{\Lambda}\mathbf{j}_s=-c^{-1}\mathbf{A}+\nabla\zeta$ [cf. (2.9)]. Hence, in virtue of (4.1) and (4.2), we have the following expression for the total current $\mathbf{j}=\mathbf{j}_s+\mathbf{j}_n$:

$$\hat{\Lambda}\mathbf{j}=-\frac{1}{c}\mathbf{A}+\nabla\zeta+\hat{\Gamma}\nabla T, \tag{4.3}$$

where $\Gamma_{ij}=\Lambda_{ik}b_{n,kj}$.

We get from (4.3) and from the equations curl $\mathbf{A}=\mathbf{H}$, curl $\mathbf{H}=4\pi c^{-1}\mathbf{j}$[36,37]:

$$\mathbf{H}=\mathbf{H}_T-c\operatorname{curl}\hat{\Lambda}\mathbf{j},\quad \mathbf{H}_T\equiv c\operatorname{curl}(\hat{\Gamma}\nabla T), \tag{4.4}$$

$$\operatorname{curl}\operatorname{curl}\hat{\Lambda}\mathbf{j}+\frac{4\pi}{c^2}\mathbf{j}=\mathbf{F}_T,\quad \mathbf{F}_T\equiv\operatorname{curl}\operatorname{curl}(\hat{\Gamma}\nabla T). \tag{4.5}$$

Evidently these are the equations that define the current $\mathbf{j}$ and the field $\mathbf{H}$ induced by the temperature gradient. In a homogeneous and isotropic medium we have $\hat{\Gamma}\nabla T=\Gamma(T)\nabla T=\Lambda b_n\nabla T$, and the terms $\mathbf{H}_T$ and $\mathbf{F}_T$ are zero. Hence, in a ring made of an isotropic material, the only entities that can exist are the current $\mathbf{j}=\mathbf{j}_s$ and the field $\mathbf{H}$ caused by the magnetic field (external field or field associated with the "frozen-in" flux). It is also evident that $\mathbf{H}_T=\mathbf{F}_T=0$ in the anisotropic case whenever ∇T coincides with the symmetry axes of the crystal.

Now let us consider a crystal plate under the conditions evident from Fig. 9 (x' and z' are the symmetry axes of the crystal); for the sake of simplicity we assume that ∇T lies in the $x'z'$ plane with the z axis lying in the direction of ∇T. Moreover, we shall be interested only in the range of temperatures close to T_c in which the effect is maximal. Here $n_s\sim T_c-T$, and we can set

$$\Lambda_{ij}=\Lambda_0\alpha_{ij},\quad \Lambda_0=\frac{m}{e^2n_s}=\frac{4\pi\delta^2}{c^2},\quad \delta^2=\delta_0^2\left(1-\frac{T}{T_c}\right)^{-1}. \tag{4.6}$$

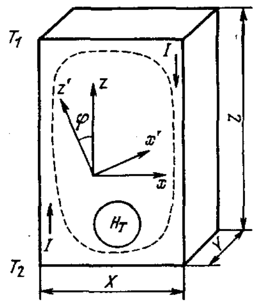

FIG. 9. Anisotropic plate. The field H_T arises in the interior of the material.

Here $\alpha_{ij}=m_{ij}/m$, or in the principal axes system we have $\alpha_{x'x'}\equiv\alpha_{x'}=m_{x'}/m$ and $\alpha_{z'z'}\equiv\alpha_{z'}=m_{z'}/m$. In this region (neat T_c) we can most probably neglect the weaker temperature dependence of the coefficients α_{ij} and $b_{n,ij}$.

Finally, let us assume that $\nabla T=$ const (in the absence of heat sources div $\hat{\varkappa}\nabla T=0$, and since the components of the heat-conductivity tensor $\varkappa_{ij}(T)$ remain finite when $T\sim T_c$, we can probably neglect the temperature dependence and anisotropy of the heat conductivity in most cases to a good degree of approximation).

With the foregoing having been taken into account, evidently the quantity $\mathbf{H}_T$ [see (4.4)] varies only slowly with z owing to the relationship $T=T(z)$. Let us assume that $\mathbf{H}_T=$ const and $\mathbf{F}_T=0$. Then, as we can easily convince ourselves, the solution of the system (4.4), (4.5) has the form $\mathbf{H}=\mathbf{H}_T+\mathbf{H}'$, $\mathbf{j}=\mathbf{j}_0e^{-x/\delta}$, where $\mathbf{H}'$ and $\mathbf{j}$ decline exponentially with x inside the specimen (see also the solution given in Ref. 8). At the boundary with the vacuum we have $\mathbf{H}=0$, i.e., we find that the field $\mathbf{H}\neq 0$ only inside the specimen; of course we assume that an external field is absent and that

$$j=j_x\sim\frac{c^2}{4\pi\delta}\frac{d\Gamma_{xx}}{dz}\frac{dT}{dz}.$$

Now let us take into account the departure from zero of the term $\mathbf{F}_T$. The increment to the current associated with it is

$$j\sim\frac{c^2}{4\pi}\frac{d^2\Gamma_{xx}}{dz^2}\frac{dT}{dz}.$$

Hence the role of the term $\mathbf{F}_T$ is small under the condition

$$\frac{\delta_0}{T_c[1-(T/T_c)]^{3/2}}\frac{dT}{dz}\ll 1.$$

The latter is satisfied even when $dT/dz\sim 0.1$°K/cm and $1-T/T_c\sim 10^{-4}$ (for tin we have $\delta_0=2.5\times 10^{-6}$ cm). Hence, under more realistic conditions, e.g., when $1-(T/T_c)\sim 10^{-2}$, we can fully assume that in the interior of the superconductor (with $\Delta x\gg\delta$) the total current $\mathbf{j}=0$. Then according to (4.4), the field in the interior of the superconductor in the case under discussion is

$$H=H_T=c\frac{d\Gamma_{xx}}{dx}\frac{dT}{dz}=\frac{4\pi}{c}\delta_0^2\frac{\alpha_{xx}b_{n,xz}+\alpha_{xz}b_{n,zz}}{T_c[1-(T/T_c)]^2}\left(\frac{dT}{dz}\right)^2$$
$$=\frac{2\pi}{c}\frac{\delta_0^2(\alpha_{z'}b_{z'}-\alpha_{x'}b_{x'})\sin 2\varphi}{T_c[1-(T/T_c)]^2}\left(\frac{dT}{dz}\right)^2. \tag{4.7}$$

Here evidently $\alpha_{x'}$, $\alpha_{z'}$, $b_{x'}$, and $b_{z'}$ are the corresponding principal values of the tensors α_{ij} and $b_{n,ij}$ that correspond to the symmetry axes x' and z'. For tin ($\delta_0=2.5\times 10^{-6}$ cm, $T_c=3.27$°K), when

$$(\alpha_{z'}, b_{z'} - \alpha_{x'}, b_{x'}) \sin 2\varphi \lessdot b(T_c) \sim 10^{11} - 10^{12} \text{ CGSE}$$

we find

$$H \lessdot \frac{10^9 - 10^{10}}{[1-(T/T_c)]^2} \left(\frac{dT}{dz}\right)^2.$$

Hence, when $1-(T/T_c) \sim 10^{-2}$ and $dT/dz \sim 0.1\,^\circ\text{K/cm}$, the field is $H \lesssim 10^{-7}-10^{-8}$ gauss.

Equation (4.7) coincides (apart from notation) with Eq. (19) in Ref. 8, but it has been derived[36] more simply and yet under more general assumptions. The estimate given in Ref. 8 indicated small values of H in agreement with the foregoing. For a reliable estimate of the field in a concrete experiment, not even contemplating a quantitative test of Eq. (4.7), one must use the experimentally determined values of the coefficients $\alpha_{z'}$, $b_{z'}$, $\alpha_{x'}$, $b_{x'}$, and δ_0 for the material employed. This especially pertains to the coefficients b_{ij}, since $\alpha_{ij} \sim 1$, while the depth δ_0 is usually well enough known. And yet, in the only experiment to observe a thermoeffect in an anisotropic superconductor,[38] the observations were compared with theory by using the values of b_{ij} calculated in Ref. 39. However, the estimate made in Ref. 39 was actually too high by several orders of magnitude.[10] Hence the conclusion appearing in Ref. 38 that theory does not agree with experiment is based on a misunderstanding. However, neither can we speak of agreement with theory, since we do not know the values corresponding to experiment of the coefficients of $(dT/dz)^2$ in (4.7).[8)] Moreover, we must bear in mind the fact that under real conditions one can observe various "parasitic" fields, in addition to the effect of (4.7). In addition to the factors cited in Ref. 38, we stress the role of inhomogeneities of the crystal (e.g., those due to deformations). As is already evident from (4.4), in an inhomogeneous specimen in which the components Γ_{ij} depend on the coordinates, a field $\mathbf{H}$ can arise that is proportional to ∇T, as has been observed in Ref. 38, at least in certain cases.[9)]

It is evident from Ref. 38 that apparently the field H_T can be directly measured, and thus Eq. (4.7) can be tested. However, it is natural to seek also other possibilities.[36] In this regard we stress, first, that the total current I flowing through the specimen

$$I = j_0 Y \delta = \frac{c}{4\pi} H_T Y, \tag{4.8}$$

can be quite large if the thickness Y of the crystal is large enough (j_0 is the current density at the surface of the crystal, and X, Y, and Z are the dimensions of the crystal. Here we assume that its thickness Y is large enough in comparison with δ; see also Fig. 9). In this regard, it is convenient to measure the current I rather than the field H_T, employing a doubly connected crystal for this purpose. Then, integrating the relationship (4.3) over the circuit with $\mathbf{j}=0$ (dashed line in Fig. 10), we obtain the flux

$$\Phi = \oint \mathbf{A} \cdot d\mathbf{l} = \Phi_T + n\Phi_0, \quad \Phi_T = H_T XZ, \quad \Phi_0 = hc/2e, \quad n = 0, 1, 2, \ldots. \tag{4.9}$$

Here we have taken Eq. (4.4) into account and have assumed in the integration that $\oint \nabla\zeta \cdot d\mathbf{l} = nh/2e$ [see (2.5)], i.e., we have at the outset taken into account the quantization of the frozen-in flux, so as not to have to return to the anisotropic case in Subsection 8. Evidently, when $n=0$ we have

$$\Phi = \Phi_T = H_T XZ. \tag{4.10}$$

Of course, here and in (4.9) the field H_T is determined by Eq. (4.7). In effect we have thus given another derivation of this formula; but if we accept (4.7), then we arrive at (4.10) simply by multiplying the field by the area XZ of the specimen.

Such a method (current measurement) is convenient, secondly, also because one can cut apart the crystal and pass the current through an auxiliary superconducting coil L (Fig. 10). The field in a coil having a large number of turns can be made considerably stronger under certain conditions than the field H_T in the main circuit. One can get an additional amplification of the effect (increase in current) by inserting a superconducting core into the aperture in the crystal (Fig. 10). (As we have stressed in subsection 3, these remarks hold also for an isotropic, inhomogeneous superconducting circuit.) Finally, the total flux Φ or the flux Φ_T can in principle prove to be so substantial that one can measure the emf that arises upon opening the circuit.

The thermoeffect in an anisotropic crystal discussed here differs from the thermoeffect associated with an inhomogeneity primarily in the quadratic dependence on ∇T (i.e., the effect (4.7)–(4.10) is proportional to $(\nabla T)^2$, whereas the field and flux in an isotropic, inhomogeneous circuit are proportional to ∇T). Moreover, the flux (4.9)–(4.10) is proportional to the dimension X, while the dimension of an ordinary superconducting thermoelectric circuit (see Fig. 4) in the direction perpendicular to ∇T plays no role (it does not increase the flux). Consequently, as we can easily see, the flux (4.10) can quite possibly prove to be larger than the flux through an inhomogeneous superconducting circuit (see subsections 2 and 3).

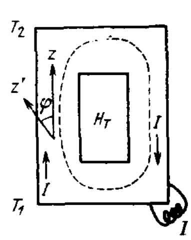

FIG. 10. Anisotropic circuit (the field H_T exists in the aperture).

8) In Ref. 28 it is concluded that the theory apparently agrees with experiment,[38] but in doing so a value of b_n is used taken from other studies, and of course, for other specimens.

9) Upon isolating the temperature factor $f(z) = (1 - T/T_c)^{-1}$ and writing $c\hat{\Gamma}\nabla T = \mathbf{a}f(z)$, we have $\mathbf{H} = \text{curl}\, \mathbf{a}f = f\, \text{curl}\, \mathbf{a} + \nabla f \times \mathbf{a}$. In the case of a homogeneous, anisotropic superconductor, we find that the vector $\mathbf{a} = \text{const}$ and $\mathbf{H}_T = \nabla f \times \mathbf{a} \sim (\nabla T)^2$. In the inhomogeneous but isotropic case the vectors $\mathbf{a}$ and ∇f are parallel, as a result of which $\mathbf{H}_T = f\, \text{curl}\, \mathbf{a} \sim \nabla T$. In the general case both terms differ from zero. We note that, in a homogeneous anisotropic metal existing in the normal state, the existence of a temperature gradient also generally gives rise to a circulating current,[40,41] but one proportional to ∇T.

II. GENERAL MACROSCOPIC THEORY BASED ON STUDYING THE ORDER PARAMETER

Above we have treated thermoelectric effect in superconductors on the basis of the two-fluid model and the London equations. It is instructive to trace how these effects are described within the framework of a more general macroscopic theory of superconductivity[42] in which the concept of a complex order parameter Ψ is introduced. Within the framework of this scheme, we shall also discuss the problem of what role the phase of the order parameter plays in describing thermoelectric effects.

5. Fundamental equations

We can conveniently base the treatment on a time-dependent phenomenological relaxation-type equation for the order parameter (cf. Refs. 43–47):

$$-\gamma\left(\hbar\frac{\partial}{\partial t}+i(\mu_n^*+e^*\varphi)\right)\Psi=\frac{1}{2m^*}\left(\hbar\frac{\nabla}{i}-\frac{e^*}{c}\mathbf{A}\right)^2\Psi+\alpha\Psi+\beta|\Psi|^2\Psi. \quad (5.1)$$

Here, as we repeat for convenience, μ_n^* is twice the chemical potential of the normal electrons,[10)] $e^*=2e$, and $m^*=2m$ are the charge and mass of the Cooper pairs, and $\mathbf{A}$ and ϕ are the vector and scalar potentials of the electromagnetic field. We can represent the right-hand side of Eq. (5.1) in the form $\delta\mathcal{F}/\delta\bar{\Psi}$, where $\mathcal{F}$ is the free energy of the macroscopic theory,[42] and α and β are the parameters that enter into this theory. An equation of the type of (5.1) in the special case of an impure, gapless superconductor is obtained from the microscopic theory,[48–50] and here one determines also the value of the dimensionless parameter γ. In the general case one must treat phenomenologically both Eq. (5.1) and the parameters that enter into it.[11)]

We shall write the expressions for the current in the system in the form

$$\mathbf{j}=\mathbf{j}_s+\mathbf{j}_n, \quad (5.2)$$

$$\mathbf{j}_s=\frac{e^*\hbar}{2im^*}(\bar{\Psi}\nabla\Psi-\Psi\nabla\bar{\Psi})-\frac{e^{*2}}{m^*c}|\Psi|^2\mathbf{A}(r,t), \quad (5.3)$$

$$\mathbf{j}_n=\sigma_n(\mathbf{E}+\mathbf{E}_{ex}^{(n)}),\quad \mathbf{E}=-\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t}-\nabla\varphi,\quad \mathbf{E}_{ex}^{(n)}=-\frac{\nabla\mu_n^*}{e^*}+\alpha_n\nabla T. \quad (5.4)$$

Here $\mathbf{j}_s$ is the ordinary superconducting current, while $\mathbf{j}_n$ is the current of the normal excitations, with σ_n and α_n being analogous to the conductivity and to the differential thermo-emf of a normal metal. (Above we have used the notation $b_n=\sigma_n\alpha_n$ and have written the thermoelectric current in the form $\mathbf{j}_n=b_n\nabla T$.) In the general case the term $\mathbf{E}_{ex}^{(n)}$ in (5.4) arises from nonequilibrium or inhomogeneity of the metal, and it can be interpreted as an extra emf of non-Coulombic origin (see Ref. 51).

Under nonequilibrium conditions in which the right-hand side of (5.1) differs from zero, as we have mentioned, we must introduce into the system under consideration also the chemical potential $\mu_s^*=\mu_n^*+\delta\mu^*$, which differs from μ_n^* (see, e.g., Refs. 52–56). The potential μ_s^* involves the phase θ of the order parameter $\Psi=Re^{i\theta}$ via the following relationship (cf. Ref. 57):

$$-\hbar\frac{d\theta}{dt}=\mu_s^*+e^*\varphi. \quad (5.5)$$

Under equilibrium conditions ($\mu_s^*=\mu_n^*=\mu^*=2\mu$, $\phi=0$) we have $-\hbar d\theta/dt=2\mu$, and the wave function (order parameter) is characterized by the simple phase factor $e^{i\theta}=e^{-2i\mu t/\hbar}$ (see Ref. 58).[12)]

Evidently the expressions (5.1)–(5.5) are invariant with respect to the gauge transformations

$$\mathbf{A}\to\mathbf{A}+\nabla\chi(\mathbf{r},t),\quad \varphi\to\varphi-\frac{1}{c}\frac{\partial\chi(\mathbf{r},t)}{\partial t},\quad \Psi\to\Psi e^{ie^*\chi(\mathbf{r},t)/\hbar c} \quad (5.6)$$

with an arbitrary (but single-valued[13)]) function $\chi(\mathbf{r},t)$ that fixes the gauge of the potentials of the electromagnetic field.[59] We see from the last transformation in (5.6) that the phase of the wave function of the superconductor varies under a gauge transformation and can be made equal to any preassigned function. The existence in (5.6) of a function χ that is arbitrary over wide limits reflects the fact that the potentials of the field and the phase are to a certain extent nonphysical quantities that we can alter for reasons of convenience. Yet, of course, the physical quantities (fields, currents, etc.) do not depend on the choice of gauge.

The relationship (5.5) allows us to establish the general form of the wave function of a nonequilibrium superconductor:

$$\Psi(\mathbf{r},t)=\exp\left[-i\int_0^t\frac{\mu_s^*+e^*\varphi}{\hbar}dt'+i\theta(\mathbf{r})\right]R(\mathbf{r},t). \quad (5.7)$$

Here $\theta(\mathbf{r})$ is a function solely of the coordinates, while $R(\mathbf{r},t)$ is the real amplitude. The representation of the wave function in the form (5.7) is convenient in the sense that the phase automatically varies in accordance with (5.6) when the potentials of the field undergo a gauge transformation.

Substituting (5.7) into (5.1) and (5.3) and separating the real and imaginary parts, we obtain the equations

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10) We note that equilibrium is established rather quickly in the system of normal electrons, so that in the discussed situations we can assume that $\mu_n=\mu$, where μ is the chemical potential of the electrons in the equilibrium or quasiequilibrium steady states. A thermodynamic analysis yields the relationships

$$\mu=\left(\frac{\partial U}{\partial n}\right)_{n_s,S}=\mu_n=\left(\frac{\partial U}{\partial n_n}\right)_{n_s,S},\quad \mu_s=\left(\frac{\partial U}{\partial n_s}\right)_{n_n,S}.$$

Here U is the internal energy per unit volume, and S is the entropy of the system. The quantity $\delta\mu=\mu_s-\mu_n$ vanishes at equilibrium, and it plays the role of the chemical potential in a system having an indefinite number of particles (e.g., a system of Cooper pairs).

11) We note that we actually do not use the concrete time-dependences for the order parameter. Hence we need Eq. (5.1) only as an example of a closed gauge-invariant scheme.

12) We note, besides, that the potential μ_s^* in (5.5) can in principle depend on v_s^2. However, as we stipulated in subsection 1, we shall nowhere write out the terms of the order of v_s^2, except in subsection 9.

13) We need the requirement of single-valuedness because the potentials of the electromagnetic field are considered to be single-valued functions of the coordinates.

$$-\gamma\hbar\frac{\partial R}{\partial t}=-\frac{\hbar^2}{2m^*}\Delta R+\frac{m^*v_s^2}{2}R+\alpha R+\beta R^3, \quad (5.8)$$

$$-\frac{2e^*}{\hbar}\gamma(\mu_s^*-\mu_n^*)R^2=\operatorname{div}\mathbf{j}_s, \quad (5.9)$$

$$\mathbf{j}_s(r,t)=e^*n_s(\mathbf{r},t)\mathbf{v}_s,\quad \mathbf{v}_s=\frac{\hbar}{m^*}\nabla\theta(\mathbf{r})+\frac{e^*}{m^*}\int_0^t(\mathbf{E}+\mathbf{E}_{ex}^{(s)})\,dt', \quad (5.10)$$

$$n_s^*(\mathbf{r},t)=\frac{1}{2}n_s=\frac{1}{2}nR^2(\mathbf{r},t),\quad \mathbf{E}_{ex}^{(s)}=-\frac{\nabla\mu_s^*}{e^*}. \quad (5.11)$$

(Here, as above, n_s^* is the pair density, n_s is the density of "superconducting" electrons, and $n=n_s+n_n$ is the total electron density.) One must supplement the above equations with the field equations (1.4) and (1.5), which give rise to the continuity equation (1.6) for the total current.

At equilibrium (when $\mathbf{j}_n=0$) we have under steady-state conditions div $\mathbf{j}_s=0$, i.e., according to (5.9), we find that the quantity $\delta\mu=\mu_s^*-\mu_n^*=0$. Under nonequilibrium conditions the normal and superconducting currents can be interconverted, and then a non-zero value of $\delta\mu^*$ arises. We shall see below (Subsection 9) that certain small dissipative effects are associated with the quantity $\delta\mu^*$.

A quasiclassical kinetic equation for the distribution function of the normal electrons (excitations) in a superconductor has been formulated[60] that holds for perturbations that vary slowly enough in time and space. The results obtained by using the kinetic treatment (see Refs. 60–68 and also Refs. 52–56) justify to a certain extent the phenomenological equations (5.1), (5.8), and (5.9), and they allow one to refine the meaning of the quantities that enter into them. In the case of rapidly varying processes, the phenomenological scheme presented above is apparently inapplicable. Then we must turn to the exact microscopic equations (see, e.g., Refs. 48–50). Since we shall be interested in slow processes, e.g., such as occur on heating a superconductor, it is convenient to start with the phenomenological equations presented above and to conduct the discussion on their basis.

6. On the meaning and role of the phase of the order parameter in the macroscopic theory of superconductivity

As we have mentioned, thermoelectric effect are sometimes associated with the phase of the order parameter. Nevertheless, we have shown in Sec. I that one can describe these effects without any use of this concept. In order to discuss in greater detail the role of the phase in the origin of the thermoelectric current in superconductors (see Subsection 7), it seems appropriate to analyze the problem of the phase in a more general form.

As we see from (5.7), the phase of the order parameter contains a certain time-independent function $\theta(\mathbf{r})$. Generally this function is not single-valued, since upon integrating around any vortex line (filament) we have

$$\oint\nabla\theta\cdot d\mathbf{l}=2\pi n,\qquad n=0,1,2,\ldots. \quad (6.1)$$

Here the number n characterizes the amount of magnetic flux $\Phi=n\Phi_0$ trapped in the vortex,[14)] where $\Phi_0=hc/2e$ is the quantum of flux. We can isolate[69] from the phase (5.7) a non-single-valued component $\theta_0(\mathbf{r})$ by writing $\theta=\theta_0+\theta_1$, where θ_0 and θ_1 are any functions that satisfy the conditions

$$\oint\nabla\theta_0\cdot d\mathbf{l}=2\pi n,\qquad \oint\nabla\theta_1\cdot d\mathbf{l}=0. \quad (6.2)$$

We can always set the single-valued component $\theta_1(\mathbf{r})$ of the phase to zero by a suitable choice of the time-independent gauge function $\chi(\mathbf{r})$ [see (5.6)]. In particular, this implies that this component of the phase has no physical meaning. We shall assume below that $\theta_1(\mathbf{r})=0$, and that $\theta=\theta_0$. Of course, this corresponds to a special choice of the gauge of the vector potential $\mathbf{A}$, in which the nonphysical part of the phase does not enter into the equations.

We see from Eq. (5.10) that the current $\mathbf{j}_s=e^*n_s^*\mathbf{v}_s$ in a superconductor in the general case consists of two components, with

$$\mathbf{v}_s(\mathbf{r},t)=\mathbf{v}_0(\mathbf{r})+\mathbf{v}_{s1}(\mathbf{r},t),$$
$$\mathbf{v}_0(\mathbf{r})=\frac{\hbar}{m^*}\nabla\theta_0(\mathbf{r}),\quad \mathbf{v}_{s1}(\mathbf{r},t)=\frac{e^*}{m^*}\int_0^t(\mathbf{E}+\mathbf{E}_{ex}^{(s)})\,dt'. \quad (6.3)$$

Upon assuming formally in (6.3) that $e^*=0$ (i.e., $\mathbf{v}_{s1}=0$), we can understand the meaning of the component of the velocity $\mathbf{v}_0(\mathbf{r})$—this quantity describes the velocity distribution in an uncharged "seed" vortex (i.e., in a vortex that would exist in an uncharged fluid). Here there is a full analogy with a vortex in superfluid He II,[6] whose velocity distribution is described by the relationship $\mathbf{V}_0=\hbar M_{He}^{-1}\nabla\theta_0$, where M_{He} is the mass of the helium atom.

This reveals the meaning of the phase $\theta=\theta_0(\mathbf{r})$ in (5.7) as the potential of the velocity of the seed vortex in the "uncharged superconductor". It is convenient to use cylindrical coordinates, in which

$$\mathbf{v}_0(\mathbf{r})=n\frac{\hbar}{m^*}\frac{\mathbf{s}}{\rho},\quad \operatorname{curl}\mathbf{v}_0=2\pi n\mathbf{h}\delta(\rho). \quad (6.4)$$

Here $\mathbf{s}$ is a unit vector along the lines of flow of the "seed" vortex, $\boldsymbol{\rho}$ is the two-dimensional coordinate which measures the distance from the axis of the vortex, and $\mathbf{h}$ is a unit vector along the axis of the vortex. The delta function on the right-hand side of (6.4) fixes the position of the axis of the vortex, while the velocity distribution in it is inversely proportional to the distance from the axis. When the charge e^* is "switched on", the term $\mathbf{v}_{1s}$ appears in (6.3), and a Meissner effect is manifested in the superconductor that leads to shielding of currents. Consequently the true velocity distribution in the vortex as found by using the field equations will no longer be described by the simple law $v_0\sim 1/\rho$, as in superfluid He II, but is determined by an exponential factor of the form $v_s\sim e^{-\rho/\delta}$, which is char-

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[14)] We treat the general case in which the vortex (or an aperture in a multiply connected superconductor) can contain n quanta of flux. Eq. (6.1) plays an essential role in introducing the concept of a "vortex filament" or "vortex".

acteristic of a superconductor.

Now let us turn our attention to the time-integrated term in the phase (5.7) and the component $\mathbf{v}_{s1}$ in (6.3). We shall assume that there are no vortices and that the non-single-valued part of the phase that describes the vortices is zero ($\theta_0(\mathbf{r})=0$, i.e., $\mathbf{v}_0=0$). Here, in the gauge that we have adopted [$\theta_1(\mathbf{r})=0$], the only component that remains in the phase of (5.7) and in Eq. (5.10) is the one containing the time integral. According to (5.10) or (6.3), the equation of motion for the velocity $\mathbf{v}_{s1}$ thus acquires the form

$$m^*\dot{\mathbf{v}}_{s1}=e^*(\mathbf{E}+\mathbf{E}_{ex}^{(s)}),\quad \mathbf{E}_{ex}^{(s)}=-\nabla\mu^*. \tag{6.5}$$

This agrees with Eq. (1.13) if we take into account the fact that the chemical potential μ_s^* in (6.5) includes the term $m^*v_s^2/2$ (see footnote 12). Evidently the velocity $\mathbf{v}_{s1}$ describes the motion of the superconducting component under the action of the applied forces $\mathbf{E}+\mathbf{E}_{ex}^{(s)}$.

Let us rewrite (6.5) in another form:

$$m^*\dot{\mathbf{v}}_{s1}=-\frac{e^*}{c}\frac{\partial\mathbf{A}}{\partial t}-\nabla(\mu_s^*+e^*\varphi). \tag{6.6}$$

If there is no inductive field (i.e., $\partial\mathbf{A}/\partial t=0$), then the velocity does not increase (steady-state condition) if

$$\mu_s^*+e^*\varphi=\text{const},\quad \nabla(\mu_s+e^*\varphi)=0. \tag{6.7}$$

The condition of constancy of the electrochemical potential (in this case, the potential $\mu_s^*+e^*\phi$) is commonly used as a condition of local quasiequilibrium in systems containing charges (see, e.g., Ref. 70).

Evidently, whenever the relationship (6.7) is obeyed, the superconducting component will be accelerated only by the inductive component $-c^{-1}\partial\mathbf{A}/\partial t$ of the electric field. This reduces the expression for the superconducting current of (5.10) [we assume that $\mathbf{A}(t=0)=0$] to a form that was adopted at one time by London and London[71]

$$\mathbf{j}_s(\mathbf{r},t)=-\frac{e^{*2}}{m^*c}n_s(\mathbf{r},t)\mathbf{A}(\mathbf{r},t). \tag{6.8}$$

In the more general gauge in which $\theta(\mathbf{r})\neq 0$, the expression for the superconducting current of (5.3) and (5.10) with account taken of (6.7) acquires the usual form

$$\mathbf{j}_s(\mathbf{r},t)=\frac{e^*}{m^*}n_s\left(\hbar\nabla\theta-\frac{e^*}{c}\mathbf{A}\right). \tag{6.9}$$

The expression for the current of the normal excitations in the superconductor (5.4) with account taken of (6.7) acquires the form

$$\mathbf{j}_n=\sigma_n\left(-\frac{1}{c}\frac{\partial\mathbf{A}}{\partial t}+\frac{\nabla\delta\mu^*}{e^*}+\alpha\nabla T\right),\ \delta\mu^*=\mu_s^{*}-\mu_n^*. \tag{6.10}$$

Evidently the expression (5.10) reduces to (6.8) or (6.9) only under the condition $\mu_s^*+e^*\phi=\text{const}$ [see (6.7)]. Otherwise a component appears in the current that depends on the time, and is not associated with the magnetic field. Hence the choice of Eqs. (6.8) and (6.9) for $\mathbf{j}_s$ is permitted only under the condition of constant electrochemical potential for the pairs $\mu_s^*+e^*\phi$.

It is interesting to compare (6.6) with the expression

$$M_{He}\dot{\mathbf{V}}_s=-\nabla\mu_{He}, \tag{6.11}$$

which Landau[72] used in the phenomenological description of the superfluidity of liquid He II. According to (6.11), the force that makes the superfluid component move is the gradient of its chemical potential, whereas in a superconductor, even when $\nabla(\mu_s^*+e^*\phi)=0$ (i.e., at quasiequilibrium), acceleration of the superconducting component of the fluid takes place (when $\partial\mathbf{A}/\partial t\neq 0$). Thus, under conditions of quasiequilibrium, the superconducting component of the current is accelerated only by the inductive component of the electric field $-c^{-1}\partial\mathbf{A}/\partial t$ [see (6.6)].

Although the electrochemical potential is constant in space under conditions of quasiequilibrium, it can depend on the time. Hence the phase factor of the wave function of (5.7) should be written in the form

$$\exp\left[-\frac{i}{\hbar}\int_0^t(\mu_s^*+e^*\varphi)\,dt'\right]. \tag{6.12}$$

We recall that above we have been dealing with a state without vortices. Hence we have assumed in (5.7) that $\theta(\mathbf{r})=\theta_0=0$. However, since the time integral in (6.12) takes into account the history of the process, this term can describe the creation and disappearance of vortices. Therefore, even if we start with a vortex-free state, then because of the multiplier (6.12) an increment $\theta_0(\mathbf{r})$ can appear in the phase that corresponds to a newly formed vortex. We shall be interested below in processes in which motion of vortices is absent (in particular, their number does not change). Hence we can set $\theta_0=0$ for $n=0$. Under equilibrium conditions ($\mu_s^*=\mu_n^*=\mu^*=\text{const}$ and $\phi=0$), the wave function of (5.7) is characterized by the usual factor $e^{-i\mu^*t/\hbar}=e^{-2i\mu t/\hbar}$ (see Ref. 58).

We can summarize what we have said above as follows. In the absence of magnetic vortices, the phase is a single-valued function of the coordinates. However, in view of the arbitrary gauge, this function has no direct physical meaning. In particular, one can always transform to a special gauge in which the phase of the superconductor is everywhere zero the London gauge of (6.8).[15] This condition fixes the value of the vector potential A. In the presence of vortices, the phase contains a non-single-valued component that can be interpreted as the velocity potential of a "seed" vortex. Moreover, under equilibrium conditions there is always the phase factor $e^{-i\mu^*t/\hbar}$; in the non-steady-state case the phase factor has the more complex form (6.12).

7. On the nature of the thermoelectric current in superconductors

The assumption (6.7) that the pair electrochemical potential $\mu_s^*+e^*\phi$ is constant is the basis of the conclusions that one sometimes encounters that thermo-

[15] We note that an analogous situation occurs in the quantum theory of gauge fields with spontaneous symmetry breaking. There a particular gauge in which the wave function becomes real also exists, while the nonphysical variables drop out of the description (the so-called Higgs phenomenon; see Refs. 73, 74).

electric effects do not exist in superconductors.[1-6] Actually, if we neglect the dissipative term $\delta\mu^* \sim \mathrm{div}\, \mathbf{j}_s$ [see (5.9)], we can write the equation for the variation in entropy per unit volume in the form[4-6]

$$\frac{\partial S}{\partial t} + \mathrm{div}\,\frac{\mathbf{q}}{T} = \frac{\Sigma}{T}. \qquad (7.1)$$

Here $\mathbf{q}$ is the heat flux, Σ is the production of entropy, and we have

$$\mathbf{q} = -\varkappa \nabla T - \sigma_n \alpha_n T \left(\mathbf{E} - \frac{1}{e^*}\nabla\mu_n^*\right), \qquad (7.2)$$

$$\Sigma = \mathbf{j}_n \cdot \left(\mathbf{E} - \frac{1}{e^*}\nabla\mu_n^*\right) - (q \cdot \nabla T)/T. \qquad (7.3)$$

Under steady-state conditions we get the following from (7.2) and (7.3) taking (5.7) into account:

$$\mathbf{q} = -\varkappa \nabla T, \quad \Sigma = -(q \cdot \nabla T)/T, \qquad (7.4)$$

i.e., the heat flux and the entropy production in the superconductor arise solely from the ordinary heat conductivity. This means that heat effects (the Thomson and Peltier heats and Joule losses) are absent in a superconductor. Yet, according to (6.7), the emf $\nabla(\mu_s^* + e^*\phi)$ that acts on the superconducting component is zero. Therefore also no potential difference exists in a heated superconductor. That is, the ordinary Seebeck effect (thermo-emf) and the associated thermoelectric current do not exist. Thus the impression can actually arise[1-6] that practically all thermoelectric effects do not exist in superconductors [apart from the small dissipative effects in (7.1)–(7.3) that involve the nonequilibrium term $\delta\mu^*$, and which lead to the convective heat transport mentioned in Subsection 2].

Moreover, we have shown in Subsection 2 that, in an inhomogenously heated closed circuit consisting of superconductors of different types, an electric current I arises together with the associated magnetic flux Φ_T. Outwardly, this phenomenon recalls the classical Seebeck effect in a normal circuit and hence the question can arise: is there not a contradiction between the statements of Refs. 1–6 and 8–15, and what is the physical nature of the superconducting current that flows around the circuit?

Before we discuss this problem, let us show that, just as in subsection 2, the existence of this effect stems from treating the expression for the total current $\mathbf{j} = \mathbf{j}_s + \mathbf{j}_n$, where $\mathbf{j}_n$ has the form [see (1.19)] $\mathbf{j}_n = \sigma_n \alpha_n \nabla T$, while $\mathbf{j}_s$ can be taken in the form of (6.8). (We assume that the frozen-in flux is absent in the ring and hence we set $\theta_0 = 0$, and moreover, that the gauge of $\mathbf{A}$ is defined by the condition $\theta_1 = 0$; thus we describe the superconductor by a real function having a phase equal to zero throughout the specimen.) Let us take into account the fact that, owing to the Meissner effect the total current is zero on a contour C lying inside the massive ring (Fig. 3b)[16]: $\mathbf{j}_s + \mathbf{j}_n = 0$, i.e.,

$$-\frac{e^*}{m^* c} n_s \mathbf{A} + \sigma_n \alpha_n \nabla T = 0. \qquad (7.5)$$

Upon integrating this relationship over the stated contour we get

$$\Phi = \oint \mathbf{A}\, d\mathbf{l} = \Phi_T, \quad \Phi_T = \frac{m^* c}{e^{*2}} \oint \frac{\sigma_n \alpha_n \nabla T}{n_s^*}\, d\mathbf{l} \neq 0, \qquad (7.6)$$

i.e., we see that actually a magnetic flux arises in a nonuniformly heated bimetallic ring, with a current flowing around the ring $I = c\Phi_T/L_s$, where L_s is the self-induction coefficient of the ring. The expression (7.6) for the magnetic flux, which was derived within the framework of the macroscopic theory that employs the concept of the order parameter $\Psi(\mathbf{r})$, coincides (when $b_n = \sigma_n \alpha_n$) with the corresponding expression (2.10) derived within the framework of the London theory. The latter is evidence of the complete equivalence of the two descriptions.[17)]

If we start not from (7.5), but from the more general expression for the current (6.9) and the condition (6.1), then we get the following expression for the flux inside the ring instead of (7.6):

$$\Phi = n\Phi_0 + \Phi_T, \quad \Phi_0 = \frac{hc}{2e}, \qquad (7.7)$$

i.e., in the general case the flux inside the ring consists of two components, namely, the flux $n\Phi_0$ that corresponds to a certain number n of flux quanta (vortices) frozen into the aperture, and the additional flux Φ_T [see (7.6)] that arises from the temperature gradient. Evidently we can associate the first term in (7.7) with the phase of the wave function, while the thermoelectric flux Φ_T is not associated with the phase, and it has [see below) a classical interpretation (moreover, we note that Planck's constant doesn't enter into the expression (7.6) for Φ_T].

Nevertheless a number of articles[10,34,77] have associated the thermoelectric current that arises in the circuit with the phase difference of the order parameter, which is assumed to arise between any two points of a heated superconductor. This interpretation is based on applying the expression (6.9) for the superconducting current and writing it in the form

$$\mathbf{j}_s = \frac{e^*\hbar}{m^*} n_s^* \nabla\Theta, \quad \nabla\Theta = \nabla\theta - \frac{e^*}{\hbar c}\mathbf{A}. \qquad (7.8)$$

Here we introduce the so-called "gradient-invariant phase" Θ. Here it is assumed that the appearance of

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[16)]In other words, we assume that the temperature T is not too close to T_c, as a result of which the condition $\delta \ll d$ holds, where d is the thickness of the specimen.

[17)]The latter also pertains to the anisotropic case that we treated in subsection 4. Upon introducing the order parameter Ψ for an anisotropic superconductor,[75,76] we have

$$j_{s,k} = \frac{e^*\hbar}{2im_k^*}\left(\bar{\Psi}\frac{\partial\Psi}{\partial x_k} - \Psi\frac{\partial\bar{\Psi}}{\partial x_k}\right) - \frac{e^{*2}}{m_k^* c}|\Psi|^2 A_k. \qquad (5.3a)$$

Here we have chosen the system of principal axes of the crystal x', y', $z' \to k = 1, 2, 3$, and of course, we do not sum over k; in the isotropic case $m_1^* = m_2^* = m_3^* = m^* = 2m$, and (5.3a) transforms into (5.3). Upon writing Ψ in the form $\Psi = \sqrt{n_s/2}e^{i\theta}$, we can easily reduce (5.3a) to the form used in subsection 4 [cf. (4.3) without the term $\hat{\Gamma}\nabla T$ and with $\zeta = \theta\hbar/e^*$; see also Ref. 36)]. As we know, Eqs. (5.3) and (5.3a) generally hold only near T_c, while at lower temperatures the relationship between $\mathbf{j}_s$ and $\mathbf{A}$ is nonlocal. However, the thermoeffects are at all significant only immediately near T_c. Hence the use of the expressions (5.3) and (5.3a) is justified in practice.

the nonzero current of (7.8) in the circuit and of the flux of (7.7) is due to the appearance of a difference in the "phases" Θ and it is proposed to measure experimentally the "phase advance" or the "thermoelectric angle" that arises on heating. In this terminology, the discussed effect acquires a quantum-mechanical ring, while the "phase" itself here appears as some really existing physical quantity, and as the reason for the appearance of the current. However, the analysis performed above (see Subsection 6) implies that no phase (and hence also no phase difference) exists as a physical quantity in the absence of vortices, and hence the cited terminology is an unfortunate choice. The fact of existence of the magnetic field and of the vector potential $\mathbf{A}$ cannot be described by a scalar function (θ or Θ).[18)] The key physical quantity in the combination Θ [see (7.8)] is precisely the vector potential. This is revealed especially clearly in transforming to the London gauge with $\theta = 0$ and writing the current in the form (6.8). Besides, the methodological remark that we have made does not affect the essence of the results obtained in Refs. 10, 34, and 77.

Thus, the above discussion allows us to conclude that the thermoelectric current in a superconducting bimetallic ring does not arise from the existence of a phase difference in the circuit, but precisely from the existence of the temperature gradient in the inhomogeneous circuit.[12] However, the problem remains unanswered here of the mechanism of appearance of the current, i.e., the problem of the forces that have set the superconducting component in motion.

We can easily understand the source of the superconducting current if we write (6.8) in the form

$$\mathbf{j}_s(t) = \frac{e^{*2}}{m^*} n_s^* \int_0^t \mathbf{E}\, dt', \quad \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{A}}{\partial t}. \tag{7.9}$$

[We recall that here $\nabla(\mu_s^* + e^*\phi) = 0$.] The following is evident from (7.9). If a field and current are initially absent in the ring [$\mathbf{A}(t=0) = 0$ for $T_1 = T_2$ and $j_s = 0$], then a superconducting current can subsequently arise only because of the appearance of the inductive accelerating force $\mathbf{E} = -c^{-1}\partial\mathbf{A}/\partial t$, i.e., because of nonstationarity. The only nonstationarity under the studied conditions involves the change in temperature of one of the ends of the specimen, e.g., T_2. Evidently, when the specimen is being heated and the temperature $T_2(t)$ varies in time, nonequilibrium sets in in the normal subsystem, and a force arises that is proportional to the temperature gradient. This force acts on the normal component and sets it is motion. Here a weak variable electric field $\mathbf{E}(t)$ is induced in the ring, and it acts on the superconducting component and causes it to accelerate. Consequently, in the ring by the time t, the current of (7.9) arises, which coincides with the London expression (6.8), together with the magnetic flux of (7.6).

[18)]Indeed, in the literature the so-called "current state" is sometimes considered in which there is a current $\mathbf{j}$, but the field $\mathbf{H} = \text{curl}\, \mathbf{A} = 0$, since $\mathbf{A} = \nabla\theta$. Evidently this description formally contradicts the field equations.

Per se the field $\mathbf{E}(t)$ is negligibly small (an estimate gives the value $\mathscr{E}(t) = \oint \mathbf{E}\cdot d\mathbf{l} \sim c^{-1}\partial\Phi/\partial t \sim 10^{-24}$ V for $\Phi \sim \Phi_T \sim 10^{-9}$ gauss$\cdot$cm^2 and $dT/dt \sim 10^{-2}$ °K/sec). However, precisely this weak field acting throughout the heating cycle (integrated over the time!)[19)] accelerates the superconducting fraction of the electrons, and this current reaches the final value of (7.9) [or (6.8)]. Subsequently this current flows by inertia without losses,[20)] and in the final state no forces act on the superconducting component. As for the normal component, we can neglect the action of the weak inductive field as compared with the normal thermo-emf $\mathbf{E}_{ex}^{(n)} = \alpha_n \nabla T$ [for tin near T_c we have the estimate $\mathscr{E}_{ex}^{(n)} = \oint \alpha_n \nabla T \cdot d\mathbf{l} \sim 10^{-8}$ V (see subsection 3), i.e., actually $\mathscr{E} \ll \mathscr{E}_{ex}^{(n)}$]. Thus, by the time t, the normal current will be

$$\mathbf{j}_n(t) = \sigma_n \mathbf{E}_{ex}^{(n)}(t) = \sigma_n \alpha_n \nabla T. \tag{7.10}$$

Thus the qualitative arguments presented above allow us to conclude that the complete circumferential current that arises in a nonuniformly heated bimetallic superconducting ring is inductive in nature.[21)] In this regard, there is an evident contrast with the analogous effect in a normal circuit (the Seebeck effect). Here, so to speak, the thermoelectric current is of a diffusion nature,[78] is directly involved with dissipative processes, and requires an emf to maintain it. Thus, there is actually no contradiction between the statements of Refs. 1–6 and 8–15, and, in fact, the effects discussed therein are different. The thermodynamic arguments[1-6] that neglect convective heat transport actually do lead to the conclusion that there is no diffusion thermo-emf nor any heat effects in superconductors, yet they do not forbid the existence in a closed ring of a nondissipative inertial current[8-15] caused by inductive electric forces. Evidently the ordinary Meissner current in a superconductor is also inductive in nature [cf. (6.8) and (7.9)] and is due to the insertion of the superconductor into a region that contains a field. In this regard, the remark we made at the end of Subsection 3 on the possible amplification of the thermoelectric current by the introduction inside the ring of a superconducting core agrees fully with the assertion of the inductive source of the discussed effect.[22)]

[19)]The integral character of the action of these forces in (5.10) and (6.3) corresponds to the situation in which the superconducting component moves without colliding with the lattice. Hence the effect of the forces is summed over the time. In the presence of collisions, the effective time of action of the accelerating force is limited to the value τ_n, or the free flight time, and the normal current will be proportional to the field $\mathbf{j} = \sigma_n(\mathbf{E} + \mathbf{E}_{ex}^{(n)})$, $\sigma_n = en\tau_n/m$, rather than to its integral.

[20)]Here we ignore dissipative effects in the superconductor that involve the regions where div $\mathbf{j}_s \neq 0$.

[21)]A detailed treatment of the mechanism of turning on the field and the dynamics of acceleration requires us to turn to the exact non-steady-state equations (5.1)–(5.7) and the field equations (1.10)–(1.12), which seems to be a rather complex problem.

[22)]We note in passing that one can explain analogously the well-known experiment [79] mentioned in connection with the discussion of whether one can consider the vector potential

In closing, let us take up briefly the experiment of Steiner and Grassman,[7] which we mention in connection with the proof of the absence of thermo-emf's in superconductors (see the Introduction). These authors suspended a bimetallic superconducting ring by an elastic filament in a weak magnetic field and then heated the ring. If a thermo-emf were to arise in the superconductor (Seebeck effect), then it should give rise to an acceleration of the superconducting electrons and to a current in the ring that increases with time, which would twist the elastic filament. However, no twisting moment was found in the system upon lengthy observation. This allowed them to state with great exactness that no accelerating force arises, and consequently they concluded that a thermoelectric current is fully absent in superconductors.[1-6] The negative result of this experiment becomes understandable if we take account of what has been said above. Actually, in Ref. 7 an increase in the electric current in the ring with time could not be observed, since an emf was actually lacking under steady-state conditions. However, if the sensitivity of the experiment[7] had been higher, then it might have been possible to detect a dc current and a magnetic field in the ring, but now caused by the accelerated electrons moving inertially. Apparently such a current has been observed in Refs. 13–15.

8. On the quantization of the magnetic flux through a ring (circuit)

The thermoelectric flux in the ring of (7.6) is proportional to the temperature difference, and naturally for this reason is not quantized. It seems expedient to discuss how this result fits with the well-known assertions on the quantization of magnetic flux in superconductors.

The concept of quantization of macroscopic motion was first introduced by Onsager for the case of superfluid He II (see Ref. 85, and also the work by Feynman[86]) and by London (Ref. 17, p. 152) for the case of superconductors (we shall find it convenient to discuss the problem of quantization for these two systems in parallel). We can easily derive the conditions of quantization by treating the expressions for the velocity of the superfluid component:

$$\mathbf{v}_s=\frac{\hbar}{M_{\rm He}}\nabla(\theta_0+\theta_1) \qquad (8.1)$$

and of the superconducting component:

$$\mathbf{v}_s=\frac{\hbar}{m^*}\nabla\theta_0-\frac{e^*}{m^*c}\mathbf{A}. \qquad (8.2)$$

Here θ_0 is the non-single-valued component of the phase of the wave function of the system, which can be interpreted as the velocity potential of the vortices (see Sec. 6). Since upon passing around the closed circuit we have the following:

$$\oint \nabla\theta_0\cdot d\mathbf{l} = 2\pi n, \qquad (8.3)$$

then we find that in He II

$$\oint \mathbf{v}_s d\mathbf{l}=2\pi n\frac{\hbar}{M_{\rm He}}, \qquad (8.4)$$

i.e., the circulation of the superfluid velocity is quantized, while in superconductors we find that

$$\oint [\mathbf{v}_s+(e^*/m^*c)\mathbf{A}]\cdot d\mathbf{l}=2\pi n\frac{\hbar}{m^*}, \qquad (8.5)$$

i.e., the so-called fluxoid is quantized.[17]

Let us examine the case of He II, in which both the normal and superfluid components of the liquid move. Here the total flux density will equal the sum of the fluxes of the two components:

$$\mathbf{J}=\mathbf{J}_s+\mathbf{J}_n=\rho_s\mathbf{v}_s+\mathbf{J}_n=\rho_s\frac{\hbar}{M_{\rm He}}\nabla\theta+\mathbf{J}_n. \qquad (8.6)$$

Here ρ_s is the mass density of the superfluid component. Upon integrating (8.6) over a closed contour or simply using (8.4), we obtain

$$\oint\frac{\mathbf{J}-\mathbf{J}_n}{\rho_s}\cdot d\mathbf{l}=2\pi n\frac{\hbar}{M_{\rm He}}. \qquad (8.7)$$

This implies that if, e.g., the liquid contains no vortices ($n=0$), then the following relationship holds:

$$\oint\frac{\mathbf{J}}{\rho_s}\cdot d\mathbf{l}=\oint\frac{\mathbf{J}_n}{\rho_s}\cdot d\mathbf{l},\qquad n=0. \qquad (8.8)$$

Let the normal flow in He II arise from the temperature gradient $\mathbf{J}_n=b\nabla T$ in such a way that the right-hand side of (8.8) differs from zero. (To do this, it suffices to take a closed, ring-shaped vessel having segments of differing cross-sections; see Refs. 12 and 35.) Then, if the temperature changes gradually, both sides of (8.8) will vary smoothly. Here the circulation of the total flow $\mathbf{J}/\rho_s$ proves to be unquantized. This situation fully agrees with the condition (8.4), according to which it is not the total flux that is quantized, but the circulation of the superfluid velocity (i.e., the number of vortices). Since the system departs from equilibrium when we apply a temperature gradient, and the fluxes $\mathbf{J}_n$ and $\mathbf{J}=\mathbf{J}_s+\mathbf{J}_n$ arise in it, then these fluxes should distribute themselves in such a way as to satisfy the quantization condition (8.4) and maintain the system, e.g., in the state $n=0$. Here, if we neglect the temperature-dependence of ρ_s, circulation of the superfluid flux is also absent, i.e., $\oint\mathbf{J}_s\cdot d\mathbf{l}=0$. Thus, the lack of quantization of the total circulating flux $\mathbf{J}$ in He II indicates only that the system is not in equilibrium, but continues to exist in a quantum macroscopic state having $n=0$.[23)]

to be a physically observable quantity.[80,81] The experiment of Ref. 79 observed a change in the current in the ring of a superconducting interferometer upon changing the flux $\Phi=\oint\mathbf{A}\cdot d\mathbf{l}$ inside the ring (see also Refs. 82–84). Under the conditions of the experiment,[79] the flux Φ was fixed by using a thin, long solenoid placed inside the ring in such a way that the magnetic field at the interferometer was zero. Consequently a rather paradoxical impression arose that the electrons "sensed" directly the vector potential $\mathbf{A}$. Yet it is clear from what has been said above that the change in the flux Φ in the solenoid was accompanied by the appearance in space of a weak inductive electric field $\mathbf{E}=-c^{-1}\partial\mathbf{A}/\partial t$ that accelerated the electrons. Thus the electrons of the superconductor reacted not directly to $\mathbf{A}$, but to non-steady-state inductive field $\mathbf{E}$.

[23)] We note that, owing to the law of conservation of angular momentum, a freely suspended ring-shaped vessel of vari-

Analogously, in the case of a superconducting ring, let us examine the law of quantization (8.5) as expressed in terms of the circulation of the total current $\mathbf{j} = e^* n_s^* \mathbf{v}_s + \mathbf{j}_n$:

$$\oint \left(\frac{\mathbf{j} - \mathbf{j}_n}{e^* n_s^*} + \frac{e^*}{m^* c} \mathbf{A} \right) \cdot d\mathbf{l} = 2\pi n \frac{\hbar}{m^*}. \tag{8.9}$$

Here, in contrast to (8.7), there is a term containing the vector potential, and moreover, the Meissner effect takes place, according to which the total current in the interior of a massive superconductor is zero.[24)] Consequently, when $n = 0$ and $j_n = \sigma_n \alpha_n \nabla T$, we shall have Eq. (7.6) with an unquantized magnetic flux instead of (8.8). Evidently the magnetic flux Φ in Eq. (7.6) is not quantized because, according to (8.5), it is not the flux that is quantized in superconductors, but the fluxoid (i.e., the circulation of the vortex velocity $v_{s0} = \hbar \nabla \theta_0 / m^*$). Only when the system is in equilibrium (i.e., when $j_n = 0$) does the magnetic flux in a massive ring prove to be quantized. Here we find from (8.9):

$$\Phi = n\Phi_0.$$

Here $\Phi_0 = hc/2e$ is the quantum of flux. (In the general case we have $\Phi = n\Phi_0 + \Phi_T$.) Thus the fact that the flux Φ_T in (7.6) and (7.7) is not quantized is characteristic of a superconductor not in a state of equilibrium (however, here the number of vortices does not change, and in this sense it is quantized as before).

As is well known, the flux is not quantized also in the case of circuits (rings, cylinders) whose thickness is of the order of or smaller than the depth of penetration δ (see, e.g., Refs. 87 and 88). There is still another possibility of getting an unquantized flux even in a massive superconductor. Namely, if the superconductor rotates with the angular velocity Ω, then at equilibrium we have

$$\mathbf{H} = \frac{2mc}{e} \mathbf{\Omega}. \tag{8.10}$$

Here e is the absolute value of the electron charge (i.e., $e > 0$). One can arrive at this result in different ways—by applying the Larmor theorem (it is not evident how to apply it in the given case) or by transforming in (1.8) to a rotating system of coordinates. Here the condition (1.9) transforms into

$$\operatorname{curl} \mathbf{v}_s = -\frac{\rho_e}{\rho m c} \mathbf{H} - 2\mathbf{\Omega},$$

where with $\mathbf{j}_s = 0$, one gets Eq. (8.10).

In the theory[42] that employs the macroscopic wave function Ψ, one can take rotation into account if one recalls that in a rotating system we have

$$\frac{m^* v_s^2}{2} = \frac{1}{2m^*} \left(\mathbf{p} - m^* [\mathbf{\Omega} \times \mathbf{r}] - \frac{e^*}{c} \mathbf{A} \right)^2.$$

Hence we must replace $\mathbf{A}$ in (6.9) by $\mathbf{A} + cm^* (\mathbf{\Omega} \times \mathbf{r})/e^*$. Upon integrating over a contour for which $\mathbf{j}_s = 0$, we arrive at the condition

$$2\pi \hbar n = \frac{e^*}{c} \Phi - 2m^* \Omega S.$$

Here S is the area of the contour, and we assume that $\Omega = \text{const}$. For the ground state in which $n = 0$, this yields Eq. (8.10), since $\Phi = HS$.

We can pose the question of how a nonequilibrium magnetic flux will relax when left by itself after suddenly removing the temperature difference. One can get a qualitative orientation toward this question by keeping the inductive term $-c^{-1}\partial \mathbf{A}/\partial t$ in the expression (6.10) for the normal current, i.e., by writing total current in the following form [cf. (6.8) and (6.9) with $\delta\mu^* = 0$]:

$$\mathbf{j} = -\frac{1}{c\Lambda} \mathbf{A} + \sigma_n \left(\alpha_n \nabla T - \frac{1}{c} \frac{\partial \mathbf{A}}{\partial t} \right). \tag{8.11}$$

The usual procedure of integration over a contour on which $j = 0$ gives the equation

$$\overline{\sigma_n \Lambda} \frac{\partial \Phi}{\partial t} + \Phi = \Phi_T. \tag{8.12}$$

Here $\overline{\sigma_n \Lambda}$ is a certain mean value of the parameter $\sigma_n \Lambda$ over the integration contour, Φ is the flux inside the contour, and Φ_T is the value of the nonequilibrium flux of (7.6). (We assume that $n = 0$; otherwise we must add the term $n\Phi_0$ to the right-hand side of (8.12). We see from (8.12) that if one creates a nonequilibrium flux Φ in a ring, then if left to itself it will decay according to the law $\Phi \sim e^{-t/\tau}$ with the characteristic relaxation time $\tau = \overline{\sigma_n \Lambda} \sim 10^{-10}$ sec (for the values $\sigma_n \sim 10^{20}$ sec^{-1} and $\Lambda \sim 10^{-30}$ sec^2). Here the system will very quickly approach the equilibrium state with $\Phi = 0$ that corresponds to the quantum state $n = 0$ (or when $n \neq 0$, to the state with $\Phi = n\Phi_0$).

We note that one can use an equation of the type of (8.12) to describe a non-steady-state thermoelectric flux generated in a ring by a time-varying temperature difference (cf. Ref. 6, p. 381). Here, according to (8.12), different types of resonance effects could arise in the circuit. However, since it is hard to produce alternating thermal gradients of high frequency (characteristic value $\tau \sim 10^{-10}$ sec), then on this level a method of generating an alternating magnetic flux in an inhomogeneous ring may prove more promising, for example by irradiating it with a sequence of sound pulses. The entrainment of the normal component that arises under the action of the ultrasound would give rise to a non-

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able cross section containing He II should begin to rotate when heated. This thermomechanical circulation effect has been discussed in Refs. 12 and 35. (Here we need not introduce the phase in the case $n = 0$ for describing the flow of He II, although this has been done in Ref. 12.) We note (see Ref. 36) that in ^{3}He and in neutron or proton fluids, when pairs having a non-zero angular momentum are produced, we must take into account the anisotropy of the fluid, especially in the presence of boundaries or of a magnetic field. This can give rise to new circulation effects caused by temperature inhomogeneity. Analogous circulation effects, though now not having any specifically quantum features at all, can probably also arise in ordinary liquid crystals.

[24)] This in particular manifests the contrast between the thermoelectric effect in superconductors and the thermocirculation effect in He II. In He II the total flux $\mathbf{J}$ in the bulk of the liquid differs from zero [owing to the arbitrariness of the contour of integration in (8.8)]. However, in the case of the superconductor, the total current density in its interior $\mathbf{j} = \mathbf{j}_s + \mathbf{j}_n = 0$, while the total current I circulating in the circuit is superconducting and flows only in the surface layer (Meissner effect).

equilibrium flux Φ_{sonic}. The problem of the steady-state acoustoelectric effect has been discussed in greater detail in Refs. 89–92. On the topic of generating a nonequilibrium flux by light (photoelectric effect) or by a flux of neutrinos, see Refs. 66 and 93.

As was noted above, in spite of the lack of quantization of a nonequilibrium magnetic flux, the system tries to conserve its state as characterized by a definite number n of vortices in the ring (in particular, the state with $n=0$). However, let us assume that we could increase without limit the nonequilibrium magnetic flux (e.g., by using a thermoelectric pile to amplify the effect;[35] see subsection 3). Then, if the field inside the ring exceeds the value $H=H_{c1}$ (where H_{c1} is the critical field that corresponds to the onset of penetration of vortices into the superconductor), this configuration of the field will prove unstable, vortices will begin to penetrate into the superconductor, and in the absence of pinning forces they will move to the periphery of the ring. Here, when the mean flux inside the ring has reached the value $\Phi_c=H_{c1}S$ (S is the area of the hole in the ring), it will no longer increase further, since the "excess" magnetic field will be "ejected" through formation of a chain of moving vortices. This dynamic pattern can arise also in a "weakly coupled" thermoelectric circuit, i.e., in the presence of a Josephson contact[25)] (Fig. 11). In this case the value of H_c is small. Hence the possibility of realization of such a non-steady state with moving vortices (see Ref. 95) seems more real. (There is also another possibility of decreasing the magnetic field in a circuit having $\Phi_T > \Phi_c$, namely, by formation of vortices of the other sign, $\Phi=\Phi_T+n\Phi_0, n<0$. Here distinctive hysteresis effects can arise in the circuit; see Ref. 35).

A "weakly coupled" circuit can also be used for detecting a thermoelectric flux $\Phi_T<\Phi_0$. For example, in the inhomogeneous circuit drawn schematically in Fig. 12 (a so-called quantum interferometer), the maximum steady-state current passing through the instrument depends on the external flux $\Phi=\Phi_e$ in the ring according to the law[82–84]

$$I_{max}=2I_0\left|\cos\frac{\pi\Phi}{\Phi_0}\right|. \tag{8.13}$$

In the presence of a temperature gradient, the total flux is $\Phi=\Phi_e+\Phi_T$. Hence the interference curve (8.13) (see Fig. 13) will be shifted in proportion to the temperature difference $\Delta T=T_2-T_1$. Since one can measure the positions of the minima in Fig. 13 to a high degree of accuracy, one could use such an apparatus in principle as a precision thermometer. However, experiments of this type have not yet been performed.

We note in closing that in principle one can observe interesting interference phenomena also in a nonuniformly heated ring-shaped vessel containing liquid He II (see Ref. 96).

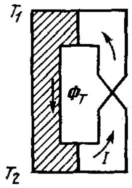

FIG. 11. Thermoelectric circuit containing a Josephson contact (schematic).

9. The thermoelectric field and the Bernoulli potential in superconductors

As before, we shall assume that the superconducting subsystem is in a state of quasiequilibrium, i.e., $\mu_s^*+e^*\phi=\text{const}$ [see (6.7)]. However, we shall reject the assumption that $\mu_s^*=\mu_n^*$, which was in fact adopted above. In other words, we shall deal with nonequilibrium effects involving the existence of the difference $\delta\mu=\mu_s^*-\mu_n^*\neq 0$. The condition of quasiequilibrium (6.7) does not assume the constancy of the electrochemical potential $\mu_n^*+e^*\phi$ for the normal component. Hence, even when $\delta\mu^*\neq 0$, as in subsection 6, we can assume that Eqs. (6.8) and (6.9) hold, and also the emf for the superconducting pairs is zero:

$$\mathcal{E}_s=\int_1^2\nabla(\mu_s^*+e^*\varphi)\cdot d\mathbf{l}=0 \tag{9.1}$$

(the integration is performed over a line that connects any two points 1 and 2). At the same time, the emf for the normal electrons differs from zero (we assume that $T=\text{const}$):

$$\mathcal{E}_n=\int_1^2\nabla(\mu_n^*+e^*\varphi)\cdot d\mathbf{l}=-\int_1^2\nabla\delta\mu^*\cdot d\mathbf{l}\neq 0. \tag{9.2}$$

A recent experiment[55] very graphically demonstrates the validity of the relationships (9.1) and (9.2). Figure 14 schematically shows an electric circuit that consists of a normal metal N and a superconductor S that exist at the same temperature T. When the steady-state current I is passed through the circuit, the normal and superconducting currents are interconverted in the region of the contact, i.e., div $\mathbf{j}_s\neq 0$. Here, according to (5.9), a non-zero nonequilibrium chemical potential difference arises: $\delta\mu_I^*=\mu_s^*-\mu_n^*$ (the subscript I on $\delta\mu$ indicates that the lack of equilibrium is caused by the current). If we measure the current in the superconducting circuit 1, 2 by using the superconducting device D (galvanometer) and the superconducting current leads 1 and 2, we get a negative result: no current passes through D [in agreement with (9.1)]. However, if we insert a normal region N_1 into the measuring circuit (see

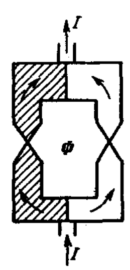

FIG. 12. Thermoelectric circuit containing two Josephson barriers (quantum interferometer). The flux in the ring is $\Phi=\Phi_T+\Phi_e$, where Φ_e is the external flux.

25) In passing we note Ref. 94, which treats the thermoelectric effect in a homogeneous ring with a Josephson barrier caused by a temperature drop at the barrier itself.

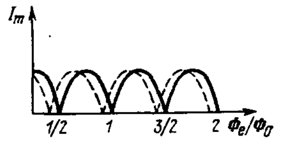

FIG. 13. Maximum current through a symmetrical interferometer as a function of the flux in the circuit (solid curve). The curve shifts (dotted curve) upon applying a temperature gradient.

Fig. 14), then a current passes through D (a voltmeter in this case) and we record a nonzero potential difference [in agreement with (9.2)].[26)]

In the case in which only a temperature gradient is present in the closed circuit, there generally also arises a nonequilibrium difference in chemical potentials $\delta\mu_T^*$ (the subscript T of $\delta\mu$ indicates that the lack of equilibrium is caused by the temperature). Taking into account the fact that under steady-state conditions we have div $(\mathbf{j}_s+\mathbf{j}_n)=0$ and adopting the expression (6.10) for $\mathbf{j}_n$, we can write Eq. (5.9) for $\delta\mu_T^*$ in the form[61]:

$$\frac{d^2\phi}{dx^2}-\frac{\phi}{l_b^2}=\beta\frac{d^2T}{dx^2}. \tag{9.3}$$

Here we have denoted $\phi=\delta\mu_T^*$, $1/l_b^2=e^{*2}\gamma/\hbar\sigma_n$, and $\beta=-e^*\alpha_n$, and we have treated the one-dimensional case. It is not difficult to obtain the solution of Eq. (9.3) by approximating the temperature distribution over the ring (Fig. 15a) as is indicated in Fig. 15b (we have unwound the ring into a rectilinear segment $-L\leqslant x\leqslant L$). Assuming that

$$\frac{dT}{dx}=-a\,\mathrm{sign}\,x,\quad \frac{d^2T}{dx^2}=a\,[\delta(x+L)+\delta(x-L)-2\delta(x)],\quad a=\frac{T_2-T_1}{L}\geqslant 0, \tag{9.4}$$

we can find the solution $\phi(x)$ in the following form[97]:

$$\phi(x)\equiv\delta\mu_T^*=\phi_1\left(\cosh\frac{L-|x|}{l_b}-\cosh\frac{x}{l_b}\right)\left(\sinh\frac{L}{l_b}\right)^{-1},\quad \phi_1=\alpha_n e^* l_b a. \tag{9.5}$$

Owing to the inhomogeneity of the ring, the quantities l_{b1} and l_{b2} can differ in different materials. Here the solution takes on a more cumbersome form[97]; Fig. 15c shows a graph of it for $l_{b1}=2l_{b2}$. Thus we find that the nonequilibrium increment $\delta\mu_T^*=\phi(x)$ arises near points where heat flows in and out of the specimen (points of change of sign of the gradient of T), and it declines exponentially away from these points with the decay length being equal to the value of l_b of the corresponding material.[27)]

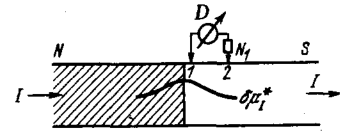

FIG. 14. Schematic diagram of an experiment[55] to observe nonequilibrium in an NS circuit containing a current.

Another nonequilibrium thermoelectric effect arises in superconductors owing to the existence of the term $\delta\mu^*_T=\phi(x)$. Namely, if we take into account Eqs. (6.7) and (9.5), we can find the electrostatic potential $\phi(x)$ = const $-\,\delta\mu^*_T$ and the thermoelectric field (see Refs. 61 and 62)

$$\mathbf{E}_T=-\nabla\varphi=\frac{\nabla\delta\mu_T^*}{e^*} \tag{9.6}$$

inside the superconductor, as well as the value of the uncompensated charge that arises from the nonequilibrium temperature distribution: div $\mathbf{E}_T=\Delta\delta\mu_T^*/e^*=4\pi\rho$. Thus an electric field exists inside a nonuniformly heated superconductor and a space charge arises (cf. Refs. 52 and 61). The appearance of the nonequilibrium increment $\delta\mu_T^*=\mu_s^*-\mu_n^*$ also leads [see (6.10)] to the additional contribution $\sigma_n\nabla\delta\mu_T^*$ to the thermoelectric current

$$\mathbf{j}_n=\sigma_n\left[-\nabla\left(\frac{\mu_n^*}{e^*}+\varphi\right)+\alpha_n\nabla T\right]=\sigma_n\,(\alpha_n\nabla T+\nabla\delta\mu_T^*).$$

This increment will be smaller by a factor of l_b/L than the current caused directly by the temperature gradient,[61,97] but it is of definite interest. The point is that if we join two points 1 and 2 having different values of $\delta\mu_T^*$ by a circuit having a normal region (similarly to what is shown in Fig. 14), then a current must flow between them. But if the connecting circuit is completely superconducting and is made of the same material as the main superconductor, then there will be no total

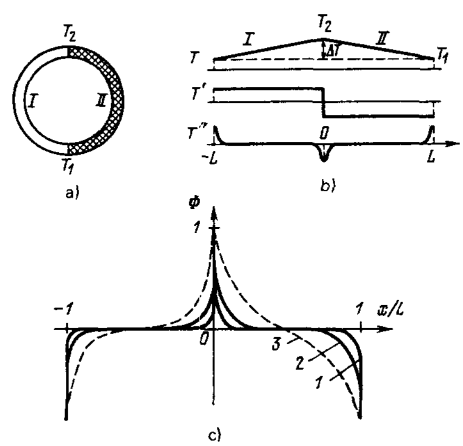

FIG. 15. Distribution of the nonequilibrium increment $\delta\mu_T^*$ in a thermoelectric ring. a) Ring; b) temperature distribution in the ring (spread out into the segment $-L<x<L$); c) distribution $\phi(x)\equiv\delta\mu_T^*(x)$.

[26)]We note that only a total current is lacking in the superconducting measuring circuit (Fig. 14), but there is a normal current [in view of (9.2)] and a compensating superconducting current such that $\mathbf{j}_s+\mathbf{j}_n=0$. This compensation is associated with the condition of quantization of the flux (see subsection 8): if flux is initially absent in the circuit, this state is conserved. Thus the condition (9.1) implies only the absence of a steady-state emf $\mathscr{E}_s$, but does not forbid the existence in the circuit of a superconducting current accelerated by inductive forces.

[27)]The kinetic approach allows one to relate the decay length l_b [or the phenomenological parameter γ in (5.9)] to the time for establishment of equilibrium between the branches of the quasiparticle spectrum of the electron-like and hole-like excitations.[52–56,61–65] According to a theoretical estimate,[61] the length l_b in the case of pure superconductors near T_c can attain values of $l_b\sim 0.1$ cm.

current. We note that one of the contact must lie in the immediate vicinity of the point where $d^2T/dx^2 \neq 0$. Otherwise the difference $\delta\mu_{T1}^* - \delta\mu_{T2}^*$ will be small, and current will be practically absent. Insofar as we know, the noted effect has not yet been observed.

We note also that the appearance of a nonequilibrium increment $\delta\mu^*$ arising from other causes should be taken into account in interpreting experiments to measure the absolute thermo-emf of metals (cf. Ref. 98) and also in discussing nonequilibrium effects in superconductors (see, e.g., Refs. 99–101). As is evident from what we have said in subsections 2 and 7, the region having div $\mathbf{j}_n = -$div $\mathbf{j}_s \neq 0$ and $\delta\mu^* \neq 0$ is responsible for convective heat transport. In this region small contributions to the Joule heat, the Peltier heat, and the Thomson thermoelectric effect should also arise.

Thus far, as we have stipulated in Subsection 1, we have not taken into account the term $\nabla m v_s^*/2$ that appears in (1.14), and essentially also in (1.11) and (1.12). But the superconducting current density $\mathbf{j}_s$ and its corresponding velocity $\mathbf{v}_s = -e^*\mathbf{A}/m^*c$ generally depend on the coordinates, and the term $\nabla m v_s^2/2$ differs from zero. Taking into account this term, or more exactly, all terms of the order of ∇v_s^2, leads to an interesting observable effect, which we shall discuss now.

Consider a superconductor existing in a constant in time external magnetic field and at a constant temperature $T=$ const. For the latter reason a normal current is lacking, and according to (1.13) and (1.14), a steady state (condition $\partial \mathbf{v}_s/\partial t = 0$) should occur under the condition

$$\mathbf{E} = -\nabla\varphi = \frac{\nabla\mu_s}{e} = \nabla\left(\frac{\mu_{s0}}{e} + \frac{mv_s^2}{2e}\right). \tag{9.7}$$

Moreover, as we know from the equations of two-fluid hydrodynamics, that, when we take terms of the order of v_s^2 into account, the potential μ_{s0} itself depends on v_s^2. Concretely (see Refs. 18–20), when $\mathbf{v}_n = 0$, we have

$$\mu_{s0}(v_s) = \mu_0 - \frac{n_n}{n}\frac{mv_s^2}{2}, \quad \mu_0 = \mu_{s0}(v_s = 0). \tag{9.8}$$

The appearance of the term proportional to n_n/n is associated with taking into account the law of conservation of momentum of all the electrons. In virtue of (9.7) and (9.8), the field that arises in the superconductor is

$$\mathbf{E} = -\nabla\varphi = \frac{\nabla\mu_s}{e} = \nabla\left(\frac{\mu_0}{e} + \frac{n_s}{n}\frac{mv_s^2}{2e}\right) = \mathbf{E}_0 + \mathbf{E}_B. \tag{9.9}$$

In the case $\nabla T = \mathbf{v}_n = 0$, the equation for the normal subsystem that is analogous to (1.13) has the form $m\partial\mathbf{v}_n/\partial t = e\mathbf{E} - \nabla\mu_{n0}$. We get from this in the steady-state case ($\partial\mathbf{v}_n/\partial t = 0$):

$$\mathbf{E} = \frac{\nabla\mu_{n0}}{e}. \tag{9.10}$$

Comparison of Eqs. (9.7)–(9.10) allows us to conclude that $\mu_{n0} = \mu_{s0} + (1/2)mv_s^2$, i.e., $\mu_n = \mu_s$, and $\delta\mu = 0$, with[28)]

$$\mu_{n0} = \mu_0 + \frac{n_s}{n}\frac{mv_s^2}{2}. \tag{9.11}$$

Thus, under steady-state conditions and when $\mathbf{H} = \mathbf{v}_s = \mathbf{v}_n = 0$, as (9.9) or (9.10) implies, the following electric field exists in an inhomogeneous superconductor:

$$\mathbf{E}_0 = -\nabla\varphi = \frac{\nabla\mu_0}{e}. \tag{9.12}$$

(Here $\mu_0 = \mu_{s0} = \mu_{n0} = \mu$ is the value of the chemical potentials when $v_s = v_n = 0$.) Of course, we have $\mathbf{E}_0 = 0$ in a homogeneous circuit. In the case of contact of two homogeneous superconductors, the field $\mathbf{E}_0$ is localized in the narrow transition region, and is associated with the appearance of a contact potential difference, in analogy with the case of normal metals.

In the presence of an external field $\mathbf{H}$, the velocity $\mathbf{v}_s \neq 0$, and we find from (9.9) or (9.10) that the following additional field arises along with the field of (9.12):

$$\mathbf{E}_B = \frac{n_s}{n}\nabla\varphi_B, \quad \varphi_B = \frac{mv_s^2}{2e}. \tag{9.13}$$

This field is due to the difference in velocities at different points of the superconductor.

The potential ϕ_B [see (9.13)] is analogous to the Bernoulli potential in the hydrodynamics of an ordinary liquid.[20] Eq. (9.13), which contains the factor n_s/n, was derived in Ref. 102 from hydrodynamic considerations and in Ref. 103 from the microscopic theory. If we neglect the dependence of μ_{s0} and μ_{n0} on v_s [see (9.8) and (9.11)] and make no distinction between μ_s and μ_n, while assuming that $\mu_s = \mu_n = \mu_{s0} = \mu_{n0} = \mu_0 = \mu$, and restrict the treatment only to the condition of equilibrium of the superconducting component of (9.7), then we obtain the following expression for the field $\mathbf{E}_B$:

$$\mathbf{E}_B = \nabla\varphi_B, \quad \varphi_B = \frac{mv_s^2}{2e}. \tag{9.14}$$

The latter differs from (9.13) by the factor n/n_s. Eq. (9.14) was derived by London (Ref. 17, p. 56), who first paid attention to the existence of the Bernoulli potential in superconductors. (A discussion of the difference between expressions (9.13) and (9.14) is also found in Refs. 104–109.)

Just like the field $\mathbf{E}_0$, the electric field $\mathbf{E}_B$ [see (9.12)] cannot be measured by a voltmeter. This is related to the circumstance that instruments of the voltmeter type actually record not the difference in electric potential, but the existence of an emf $\mathscr{E} = \int_1^2 \nabla(\phi + \mu/e)\cdot d\mathbf{l}$ in a circuit, i.e., they measure the difference in chemical potential $\mu + e\phi$ that arises in the circuit under nonequilibrium conditions.[104] Actually, a current does not pass through a conductor that joins the two points

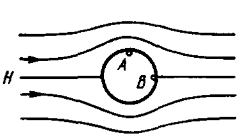

FIG. 16. Superconductor in an external field. The velocities v_s and the kinetic energies $m^*v_s^2/2$ differ at the points A and B (owing to the inhomogeneity of the field). Consequently the equilibrium conditions of the system are altered and a Bernoulli potential arises.

[28)]We can also derive the expressions (9.8) and (9.11) for μ_{s0} and μ_{n0} directly by considering the equations of motion for $\mathbf{v}_s$ and $\mathbf{v}_n$ (see Ref. 18, Sec. 2.5, and also Refs. 19 and 20) and the conditions of equilibrium with the field $\mathbf{E}$ taken into account.

A and B of a superconductor having different values of $mv_s^2/2$ (Fig. 16), owing to the equality of the electrochemical potentials $\mu_s^* + e^*\phi = \text{const}$ and $\mu_n^* + e^*\phi = \text{const}$ at these points [compare Eqs. (9.1) and (9.2) with $\delta\mu^* = 0$]. However, one can measure the electric field $\mathbf{E}_B$ by a contactless method by using a capacitative circuit.[105,106] Experiment[106] confirms the relationship (9.13), which contains the factor n_s/n. According to (9.13), the field does not depend on the temperature (since the factors n_s and $v_s^2 \sim \delta^2 \sim 1/n_s$ cancel out in (9.13),[29)] as is observed experimentally. The magnetic field that gives rise to the potential difference under the conditions of the experiments[105,106] could either be fixed externally[105] or created by a current passed through the specimen.[106] The potential difference detected in Refs. 105 and 106 reached values of the order of 10^{-8} V.

In the general case involving nonequilibrium ($\nabla T \neq 0$) and a magnetic field $\mathbf{H}$ (i.e., $\mathbf{v}_s \neq 0$), it is not difficult to convince ourselves that the total electric field is the sum

$$\mathbf{E} = \mathbf{E}_0 + \mathbf{E}_B + \mathbf{E}_T.$$

Here $\mathbf{E}_0$ is the field of (9.10) involving inhomogeneity, $\mathbf{E}_B$ is the Bernoulli field of (9.13), and $\mathbf{E}_T = \nabla\delta\mu_T^*/e^*$ is the thermoelectric field of (9.6).

Finally we mention another electrostatic effect (see, e.g., Refs. 6,110) that gives rise to an electric field, but doesn't create an emf. Namely, in the case of an open circuit under the condition $\mu + e\phi = \text{const}$ and in the presence of a temperature gradient, an electric field arises in a superconductor owing to the appearance of an increment of the chemical potential $\delta\mu = (\partial\mu/\partial t)dT$. Attempts to observe this field have been undertaken in Refs. 25, 111, and 112.

CONCLUDING REMARKS

We hope that we have made the fact plain enough that thermoelectric phenomena in the superconducting state not only do not vanish, but even, in principle, are quite multifaceted. It is true that the pertinent effects (fields, currents) are generally very small in comparison with those that occur in the normal state; hence they have not been observed in the past. However, the development of measuring technique has made the observation of thermoelectric effects in superconductors quite possible, and properly speaking, the pertinent experimental studies have already begun. We can suppose that in the next few years this field will attract more attention, and a number of interesting results will be obtained. The major goal of this article consists precisely in illuminating the present state of the problem, and in particular, its physical content, thus enabling the development of experimentation. Very broad potentialities along this line exist both in regard to inhomogeneous circuits or bimetallic plates made of isotropic superconductors (subsections 2 and 3) and in the case of anisotropic (noncubic) monocrystalline superconductors (subsection 4). Of course, the effects discussed in Sec. 9 also merit attention.[30)]

But we shall not repeat here what we have said above in the pertinent sections, and shall only make a comment of a more general nature.

For many years (four decades!) the study of superconductivity has concentrated on thermodynamic equilibrium conditions, or somewhat more exactly, on superconductors at a temperature T that has become established and is everywhere the same. Evidently this means that for a given material the distribution function of both the electrons and the phonons is fully determined by a single number T. Yet under nonequilibrium conditions, the state is characterized by the above-mentioned two functions, whereby in principle an immeasurable number of new possibilities is opened up. Heat transport (heat conductivity), absorption of sound, and thermoelectric effects in superconductors belong to the category of nonequilibrium phenomena in their simplest (in a certain sense) variant, in which the temperature of the electrons and the phonons is the same, and primarily, characterizes the state of the metal locally, but varies from point to point. But, of course, even the aforementioned situation occurs only in the case of a sufficiently small mean free path. As this mean free path increases, and especially when "normal" electrons (quasiparticles) are injected through the boundary or by illumination, we pass into the region of states that are no longer describable by quasiequilibrium distribution functions with a temperature $T(r, t)$. Here we can encounter situations that are quite unusual (within the framework of equilibrium concepts). As the most striking example, let us point out that under an inverted population of the electronic levels, superconductivity can arise not in the case of attraction, as is usual, but in the case of repulsion between the electrons.[113,114] We can suppose that the study of nonequilibrium states of superconductors will in time play an ever greater role in the field of superconductor physics.[31)] Thermoelectric effects already under quasiequilibrium conditions belong to this same field of phenomena, while under sharply nonequilibrium conditions they are also both of independent interest, and perhaps, can be used to study (and measure) other nonequilibrium phenomena. In view of what has been said, we do not doubt that theoretical and experimental studies of ther-

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[29)]Actually, since $\mathbf{H} = \text{curl } \mathbf{A} \sim \mathbf{A}/\delta$, we have $\mathbf{A} \sim \mathbf{H}\delta$, where δ is the London penetration depth. Taking into account the fact that $\mathbf{j}_s = en_s\mathbf{v}_s$, we can rewrite Eq. (6.8) in the form $\mathbf{v}_s = e\mathbf{A}/mc$, whence we bet $v_s^2 = (e/mc)^2H^2\delta^2$. Since $\delta^2 = mc^2/4\pi e^2 n_s$ [see (2.7)], we have $v_s^2 \sim 1/n_s$, and when we neglect the dependence of n_s and n_n on the coordinates, the temperature-dependence drops out in (9.13).

[30)]Many other effects have not been discussed at all. In particular, we have completely put aside the very interesting nonsteady-state thermoelectric and thermomagnetic effects involving moving vortices.

[31)]As it seems to us, two other very important fields of superconductivity physics of tomorrow will be studies in the fields of high-temperature and surface superconductivity.[114]

moelectric effects in superconductors have a great future.

In conclusion, the authors take the opportunity to thank L. P. Pitaevskiĭ and A. A. Sobyanin for remarks made upon reading the manuscript.

NOTATION

$e^* = 2e$ – charge of a Cooper pair;
$m^* = 2m$ – twice the mass of an electron;
μ_s – chemical potential of the superconducting subsystem;
μ_n – chemical potential of the "normal" subsystem;
$\mu_s^* = 2\mu_s$, $\mu_n^* = 2\mu_n$;
$\delta\mu^* = \mu_s^* - \mu_n^*$ – nonequilibrium difference in chemical potentials;
$\mathbf{j}_s$ – superconducting current density;
$\mathbf{j}_n$ – current density of the normal excitations;
$\mathbf{j} = \mathbf{j}_s + \mathbf{j}_n$ – total current density in the superconductor;
$\mathscr{E}$ – electromotive force;
b – thermoelectric coefficient of the normal metal;
b_n – thermoelectric coefficient of the normal excitations of the superconductor;
σ_n – normal conductivity of the superconductor;
$\alpha_n = b_n/\sigma_n$ – differential "thermo-emf";
H_T – thermoelectric magnetic field arising in a superconducting ring;
Φ_T – thermoelectric magnetic flux arising in a superconducting ring;
$\Lambda = 4\pi\delta^2/c^2$ – parameter of the London theory;
$\delta = (m^*c^2/4\pi e^2 n_s^*)^{1/2}$ – London depth of penetration;
n_s – density of "superconducting" electrons;
$n_s^* = (1/2)n_s$ – density of Cooper pairs;
n_n – density of "normal" electrons;
$\Phi_0 = hc/2e \approx 2\times10^{-7}$ gauss·cm^2 – quantum of flux;
$\mathbf{A}, \phi$ – vector and scalar potentials of the electromagnetic field;
χ – arbitrary gauge function;
$\Psi = Re^{i\theta}$ – complex order parameter.

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