Thermoelectric effects in the superconducting state

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The thermoelectric effects which may be observed in the superconducting state are considered. The circulation heat transfer and the appearance of a thermoelectric superconducting current in anisotropic superconductors and in a superconducting thermoelectric circuit are discussed specifically. The special nature of the thermoelectric effects in high-temperature superconductors is stressed.

Thermoelectric effects in superconductors began to attract attention back in the late twenties (for a review see Ref. 1). A conclusion was then reached that "all the thermoelectric effects disappear in the superconducting state" (see Ref. 1). A similar view was held widely and, for example, in a book[2] published in English in 1969 and in the Russian translation in 1972, the authors say: "It is found, both from theory and experiment that thermoelectric effects do not occur in a superconducting metal. For example, no current is set up around a circuit consisting of two different superconductors if the two junctions are held at different temperatures below their transition temperatures." It would seem that we are dealing with quite categorical statements. However, strictly speaking these statements are not true: the thermoelectric effects do not disappear in the superconducting state and, in particular, in the superconducting circuit just mentioned there is a current I_s. However, we are not simply dealing here with an error but with the fact that I_s under normal conditions would have been several orders of magnitude lower than the current I_n expected in the same circuit for two metals in the normal state. More specifically, if we speak of a circuit made of a wire with a diameter d, then $I_s/I_n \propto (\delta/d)^2$, where δ is the depth of penetration of the magnetic field into the superconductor; for example, if $\delta \sim 10^{-5}$ cm and $d \sim 0.1$ cm, then obviously $I_s/I_n \sim 10^{-8}$. Therefore, the thermoelectric current I_s could be detected in a superconducting state only by modern methods of measuring the magnetic field, whereas in the usual investigations of the thermoelectric effects[1] this current cannot be detected. The existence of a thermoelectric current I_s in a completely superconducting circuit is naturally interesting for its own sake. However, this is not the end of the story: some other effects of thermoelectric origin can appear in the superconducting state. The fact that the thermoelectric effects do not disappear in the superconducting state was pointed out back in 1944 (Ref. 3). However, for a long period of 30 years (!) the thermoelectric effects in superconductors have attracted practically no attention and only in 1974 there appeared several theoretical and experimental papers on this topic (for a bibliography see the review in Ref. 4). One might expect that the ice was broken, but there have been no extensive investigations of the subject. Undoubtedly, it is not easy to observe the thermoelectric effects in the superconducting state (for reviews see Refs. 4 and 5). Moreover, there are some ambiguities in the experimental situation. This will be discussed later, but at this point I shall simply say that the lack of interest in the subject is incomprehensible. There is some hope for a change in this situation, particularly since certain special features of the thermoelectric effects in high-temperature superconductors have been revealed.[6,7] The present paper, like the recent communication[7] and a conference paper[8] (which are not very readily accessible to Soviet readers), were written to draw attention to the thermoelectric effects in superconductors or, more exactly, in the superconducting state. However, the purpose is not to provide in any sense a comprehensive review covering all aspects.

1. It is appropriate to recall here the thermoelectric effect in a circuit of two metals I and II which are in the normal state (Fig. 1). Obviously, if the metals are superconductors, then the minimum temperature T_1 in this circuit should exceed the critical temperatures of both metals $T_{c,I}$ and $T_{c,II}$. Naturally, it is assumed that there is no external magnetic field because if there is such a field the metals may be in the normal state even if $T < T_{c,I,II}$. We shall always assume that there is no external magnetic field.

The local current density $\mathbf{j}$ is related to the intensity of an electric field $\mathbf{E}$ and a temperature gradient ∇T by

$$\mathbf{j} = \sigma\left(\mathbf{E} - \frac{\nabla\mu}{e}\right) + b\nabla T, \tag{1}$$

where μ is a suitably normalized chemical potential (e is the electron charge). From now on we shall sometimes omit the term with $\nabla\mu$ (because it is unimportant for a closed circuit) and we shall ignore the signs. If a conductor is anisotropic, then in the local approximation we have

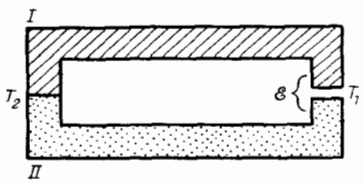

FIG. 1. Circuit consisting of two metals I and II which are in the normal state.

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$$j_i = \sigma_{ik}\left(E_k - \frac{\partial\mu/\partial x_k}{e}\right) + b_{ik}\frac{\partial T}{\partial x_k}. \quad (2)$$

If the circuit of the type shown in Fig. 1 is open, then $\mathbf{j} = 0$ and integration of Eq. (1) along the circuit gives the thermo-emf at the "cut" (i.e., at the contacts of the open circuit):

$$\mathscr{E} = \oint \mathbf{E}\,d\mathbf{s} = \oint\left(\frac{b}{\sigma}\right)\nabla T\,d\mathbf{s} = \int_{T_1}^{T_2}\left[\left(\frac{b}{\sigma}\right)_{\mathrm{II}} - \left(\frac{b}{\sigma}\right)_{\mathrm{I}}\right]dT. \quad (3)$$

The coefficient $S(T) = b(T)/\sigma(T)$ is known as the thermoelectric power or the Seebeck coefficient (instead of S many authors use α). The transport coefficients b and σ (the latter represents the conductivity) have been the object of investigations in the physics of metals and semiconductors. Within the framework of the electron gas or Fermi liquid models the coefficients b and σ are determined by the nature of the Fermi surface and by the distribution function of electrons or of corresponding quasiparticles (see, for example, Refs. 9–11). Therefore, naturally, information on the function $b(T)$ or, in the anisotropic case, on the tensor $b_{ik}(T)$ is very interesting. There is an extensive literature (see Refs. 1 and 9 and the bibliographies given there) on determination of the function $S(T)$ for superconductors in the normal state. This applies also to high-temperature superconductors (see, for example, Refs. 1 and 12–17). Naturally, we must distinguish the normal state in the absence of an external magnetic field (i.e., at temperatures $T > T_c$) and the normal state in a field higher than the critical value.

We shall now consider a mixed circuit in which part of the metal is superconducting. Let us assume specifically that $T_{c,\mathrm{II}} < T_{c,\mathrm{I}}$ and that the critical temperature $T_{c,\mathrm{II}}$ of the metal II is less than the temperatures T_2 and T_1 at the end of the circuit (Fig. 2). In this situation the metal I is in the normal state in the interval between the temperatures T_2 and $T_{c,\mathrm{I}}$. It follows from experiments that the emf developed in this circuit is

$$\mathscr{E} = \int_{T_{c,\mathrm{I}}}^{T_2}\left(\frac{b}{\sigma}\right)_{\mathrm{I}} dT. \quad (4)$$

If the whole circuit becomes superconducting (i.e., if $T_2 \leqslant T_{c,\mathrm{I}}$), then the thermo-emf $\mathscr{E}$ disappears, which is formally clear also from Eq. (4). This is the result stated at the beginning of this paper: there are no thermoelectric effects in a superconducting circuit (in addition to the thermo-emf, also the Peltier heat and the Thomson effect also disappear in such a circuit, as follows from the experiments reported in Ref. 1).

The proof of the absence of the thermo-emf in a superconductor was assumed to be provided also by the experiments reported in Ref. 18, where to a high degree of precision it was concluded that the heating of one of the junctions of a closed superconducting circuit produced no current rising with time. The question is: what follows from this experiment? To some approximation, a change in the density of the superconducting current can be described by the following equation (sometimes called the second London–London equation)

$$\frac{\partial\Lambda\mathbf{j}_s}{\partial t} = \mathbf{E} - \frac{\nabla\mu}{e}, \quad (5)$$

where in the adopted approximation we have $\Lambda = 4\pi\delta^2/c^2$ and $\delta(T)$ is the depth of penetration of a weak magnetic field into a superconductor.

Since the current density $\mathbf{j}_s$ does not rise in this experiment, it follows from Eq. (5) that in the presence of a temperature gradient in a superconductor, we have

$$\mathbf{E} - \frac{\nabla\mu}{e} = 0. \quad (6)$$

2. If we substitute Eq. (6) into Eq. (1) and assume that $\mathbf{j} = 0$, we reach the conclusion that in the superconducting state we have $b = 0$. However, there are no grounds for reaching this conclusion and, which is most important, the relationship (1) is invalid in the superconducting state. It must be recalled, as pointed out back in 1943 (Ref. 3), that two currents flow in a superconductor: the superconducting current of density $\mathbf{j}_s$ and the normal current of density $\mathbf{j}_n$. This is in full analogy with the superfluid and normal flows in He II.

The normal current is carried by "normal" electrons (excitations) and it does not differ essentially from the current in the normal state of a metal. Therefore, in a superconductor the relationship (1) applies to $\mathbf{j}_n$:

$$\mathbf{j}_n = \sigma_n\left(\mathbf{E} - \frac{\nabla\mu}{e}\right) + b_n\nabla T. \quad (7)$$

Therefore, under the conditions corresponding to Eq. (6), we have

$$\mathbf{j}_n = b_n\nabla T. \quad (8)$$

At $T = T_c$ a second-order transition takes place so that there are no grounds for expecting discontinuities of the functions $\sigma(T)$ and $b(T)$, i.e., $b_n(T_c) = b(T \to T_c)$, where $b(T)$ refers to the normal state. If we ignore fluctuations, we can expect these functions to have only a discontinuity of the derivative with respect to T at $T = T_c$. Cooling, when the "normal electrons" are "frozen out" in the superconducting state, lowers the value of $\sigma_n(T)$ right down to $\sigma_p(0) = 0$ (in the presence of the superconducting gap). The value of $b_n(0)$ also vanishes and in the simplest case the function $b_n(T)$ falls monotonically on reduction in T. However, in the "exotic" pairing case, the function $b_n(t)$ varies nonmonotonically and can increase strongly in a certain range of temperatures.[19,20] We shall return to this point later.

It therefore follows that below T_c under steady-state conditions when Eq. (7) should be obeyed, if $\nabla T \neq 0$, the density of the normal current $\mathbf{j}_s$ should be finite because of Eq. (8). However, if the circuit is open, then the total current is zero and in the simplest case the density of the total current also vanishes: $\mathbf{j} = \mathbf{j}_s + \mathbf{j}_n = 0$, i.e.,

$$\mathbf{j}_s = -\mathbf{j}_n = -b_n\nabla T. \quad (9)$$

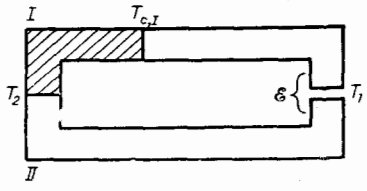

FIG. 2. Circuit in which only a part of the metal I (shown shaded) is in the normal state; the rest of the circuit is in the superconducting state.

In the case of a homogeneous[1)] and isotropic superconductor such a solution should indeed be correct: it satisfies the equations of the problem. These equations are in the simplest case as follows (for details see, for example, Ref. 4):

$$\operatorname{curl} \mathbf{H} = \frac{4\pi}{c}\mathbf{j} = \frac{4\pi}{c}(\mathbf{j}_s + \mathbf{j}_n),$$
$$\operatorname{curl} \Lambda \mathbf{j}_s = \Lambda \operatorname{curl} \mathbf{j}_s + [\nabla\Lambda, \mathbf{j}_s] = -\frac{1}{c}\mathbf{H}. \tag{10}$$

Hence, in view of the condition div $\mathbf{H} = 0$, we have

$$\nabla\mathbf{H} - \frac{4\pi}{\Lambda c^2}\mathbf{H} = -\frac{4\pi}{c}\operatorname{curl}\mathbf{j}_n + \frac{4\pi}{c\Lambda}[\nabla\Lambda, \mathbf{j}_s]. \tag{11}$$

The material is assumed to be isotropic (because otherwise Λ should be replaced with a tensor Λ_{ij}; see Refs. 3 and 4 and the discussion given below). Next, for a homogeneous material we have $\nabla\Lambda = 0$ and curl $\mathbf{j}_n = \operatorname{curl}(b_n(T)\nabla T) = 0$, and it then follows from Eq. (10) that the magnetic field $\mathbf{H}$ decays with depth in the metal in the manner usual for a superconductor. Well inside the metal we have $\mathbf{H} = 0$ and, obviously, it follows formally from Eq. (11) that the total current density indeed vanishes: $\mathbf{j} = \mathbf{j}_s + \mathbf{j}_n = 0$.

3. Therefore, if we consider a rod made of a homogeneous and isotropic superconductor (Fig. 3), then under steady-state conditions, we find that

$$\mathbf{j}_s = -\mathbf{j}_n = -b_n\nabla T, \quad \mathbf{E} - \frac{\nabla\mu}{e} = 0, \quad \mathbf{H} = 0. \tag{12}$$

For the same rod but in the normal state, we obtain

$$\mathbf{j} = 0, \quad \left(\mathbf{E} - \frac{\nabla\mu}{e}\right) = -b\nabla T. \tag{13}$$

The appearance of a "convective" current is far from self-evident and it gives rise to an additional transport of heat by the normal current. In the normal state when $\mathbf{j} = 0$ the flow of heat (we are ignoring the signs) is

$$\mathbf{q} = \varkappa\nabla T, \tag{14}$$

where $\varkappa$ is the thermal conductivity.

In the case of a normal metal, to a good approximation, we have

$$\varkappa = \varkappa_{ph} + \varkappa_{el}, \tag{15}$$

where $\varkappa_{ph}$ is that component of $\varkappa$ which is associated with the lattice (phonons) and $\varkappa_{el}$ is the electron component of the thermal conductivity.

In the superconducting state, we have

$$\varkappa = \varkappa_{ph} + \varkappa_{el} + \varkappa_c, \tag{16}$$

where $\varkappa_{el}$ is defined, for example, assuming that $\mathbf{j}_n = 0$, whereas $\varkappa_c$ allows for the "circular" transport of heat which is due to the presence of the current $\mathbf{j}_n$. However, the main contribution to $\varkappa_c$ is not simply related to the thermal conductivity in the bulk of the metal, but to the conversion of $\mathbf{j}_n$ into $\mathbf{j}_s$ and back again at the ends of the rod (Fig. 3).

The existence of the circular thermal conductivity in the superconducting state was pointed out back in Ref. 3, but

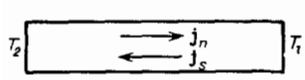

FIG. 3. Rod made of a superconductor. At $T < T_c$ there are two opposite currents with densities $\mathbf{j}_s$ and $\mathbf{j}_n = -\mathbf{j}_s$.

at that time it was not possible to calculate $\varkappa_c$ because it required a microscopic theory of superconductivity established only in 1957 and later. Some calculations have been carried out earlier[21] and were then repeated on the basis of the BCS theory.[22]

We shall give an estimate of $\varkappa_c$ due to the conversion of $\mathbf{j}_n$ into $\mathbf{j}_s$ (this is the main contribution). At the ends of the rod (at temperatures $T = T_2$ and $T = T_1$) the formation and dissociation of a pair releases or absorbs an energy $2\Delta(T)$, where $\Delta(T)$ is the gap width per one electron. The density of the normal current is $\mathbf{j}_n = en_n\mathbf{v} = b_n\nabla T$, where e is the electron charge and n_n is the density of the normal electrons (quasiparticles). It is therefore clear that at the end of the rod the energy released per unit time is of the order of $\Delta(T)n_n v = j_n\Delta/e = b_n\Delta(\nabla T)/e$, but this is in fact the heat flux $q_c = \varkappa_c\nabla T$. Hence, $\varkappa_c \propto b_n\Delta(T)/e$. It then follows from the Wiedemann–Franz law that

$$\varkappa_{el} = \frac{\pi^2 k_B^2}{3e^2}T\sigma_n; \tag{17}$$

here, $\sigma_n = j_n/\mathrm{E}$ is the conductivity due to the normal electrons introduced above [see Eq. (7)].

Combining the above expressions, we obtain

$$\frac{\varkappa_c}{\varkappa_{el}} \sim \frac{3eS_n\Delta}{\pi^2 k_B^2 T} \sim \frac{\Delta(T)}{E_F} \sim \frac{k_B T_c}{E_F}, \tag{18}$$

where in the derivation of the penultimate expression we used

$$S_n = \frac{b_n}{\sigma_n} = \frac{\pi^2 k_B^2 T}{3eE_F}, \tag{19}$$

which is valid for free electrons whose energy is E_F (see, for example, Sec. 6.1 in Ref. 10); naturally, on transition to the last expression in Eq. (18) it is assumed that we are speaking here of a region near T_c, as a result of which we find that $\Delta(T) \sim \Delta(T_c) \sim k_B T_c$.

We obviously used above the model of Bardeen, Cooper, and Schrieffer (BCS) and assumed that the normal electrons are free [Eq. (19)]. However, the thermoelectric effects are sensitive to the distribution function of the normal electrons and even the estimate given by Eq. (18) is only rough.

If we nevertheless use Eq. (18), we find that in the case of "ordinary" superconductors with $T_c \sim 1$–10 K and $E_F \sim 3$–10 eV, we have

$$\frac{\varkappa_c}{\varkappa_{el}} \sim 3\cdot 10^{-4}. \tag{20}$$

Under these conditions the circulation thermal conductivity is of no interest. The situation has changed drastically since the discovery of high-temperature superconductors which have higher values of T_c and lower values of E_F. For example, if $T_c \sim 100$ K and $E_F \sim 0.1$ eV, we now have[8]

$$\frac{\varkappa_c}{\varkappa_{el}} \sim 0,1. \tag{21}$$

In view of the roughness of the estimate given by Eq. (18), we may indeed find that in the case of some materials the inequality $\varkappa_c/\varkappa_{el} \gtrsim 1$ may be satisfied. Then, if pairing is not of the s type, as in the BCS theory, but of the p or d type and, in general, if it is exotic pairing, then $\varkappa_c/\varkappa_{el}$ increases by a factor $E_F/k_B T_c$ (Refs. 19 and 20) and, therefore, even if we adopt the estimate given by Eq. (18), we may find that $\varkappa_c/\varkappa_{el} \sim 1$. The situation in the case of high-temperature superconductors is similar to that of heavy-fermion supercon-

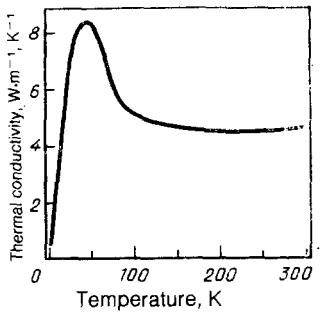

FIG. 4. Temperature dependence of the thermal conductivity of the high-temperature superconductor $YBa_2Cu_3O_{7-y}$.

ductors.[23] In the latter case both T_c and E_F are low, so that $\varkappa_c/\varkappa_{el} \gtrsim 1$. Moreover, in contrast to high-temperature superconductors, the exotic pairing is very likely in heavy-fermion superconductors.

4. The appearance of the circular thermal conductivity should obviously increase the total thermal conductivity in the superconducting state compared with the thermal conductivity $\varkappa_{ph} + \varkappa_{el}$. At the same time, $\varkappa_{el}$ falls as a result of cooling, because the normal electrons become "frozen out." However, the value of $\varkappa_{ph}$ may even increase as a result of cooling because of the weaker scattering of phonons by electrons. Consequently, both $\varkappa_{ph}$ and $\varkappa$ exhibit a maximum at $T < T_c$. Such a maximum had been observed a long time ago (see Refs. 1 and 21). In the case of high-temperature superconductors the appearance of a maximum is the rule rather than the exception. By way of example, we reproduced in Fig. 4 the dependence $\varkappa(T)$ based on Ref. 24: it applies to a high-temperature superconductor of the 1–2–3 type ($YBa_2Cu_3O_{7-y}$). Since in the case of high-temperature superconductors the contribution $\varkappa_c$ may be large, as demonstrated above, in this case it is quite realistic to ask the question: what is the mechanism responsible for the rise of $\varkappa$ at $T < T_c$? Are we speaking here of the contribution of $\varkappa$ or the rise of $\varkappa_{ph}$? There is as yet no answer to this question and a detailed theoretical and experimental analysis will be needed to obtain it. It would be very useful to carry out measurements of the thermal conductivity of single crystals. Then, instead of $\varkappa$ we have the tensor $\varkappa_{ik}$ (we have in mind here crystals with symmetry less than cubic). Specifically, in the case of the 1–2–3 high-temperature superconductors and other strongly anisotropic materials it will be necessary to determine $\varkappa(T)$ for the heat flowing along the c axis and in the (a, b) plane (in this plane the anisotropy of $\varkappa$ is probably very weak and it should be altogether absent in the case of tetragonal symmetry). We can expect the anisotropy of $\varkappa_{ph}$ to be considerably less than the anisotropy of $\varkappa_{el}$ and $\varkappa_c$. Measurements of $\varkappa$ of single crystals have already been made;[25] we should mention here also other measurements of the thermal conductivity of high-temperature superconductors.[26–29] In addition to revealing the role of anisotropy, it may be useful to study the role of impurities and defects (particularly, those created by neutron irradiation—see Ref. 29), strains, and of an external magnetic field.

5. The exact compensation of the current densities $\mathbf{j}_s$ and $\mathbf{j}_n$, i.e., the situation described by Eq. (9), occurs in general only in isotropic and homogeneous superconductors (see Sec. 2). In the case of inhomogeneous but isotropic or

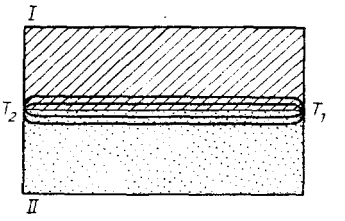

FIG. 5. Bimetal plate. The resultant superconducting current $\mathbf{I}_s$ flows in a layer of thickness of the order of δ near the interface or "junction" between the metals I and II.

even homogeneous and anisotropic superconductors (more exactly when the tensor Λ_{ik} cannot be reduced to $\Lambda\delta_{ik}$ and the direction of ∇T does not coincide with one of the symmetry axes of a crystal), the exact compensation is not obtained and a certain resultant superconducting current I_s appears. Although both possibilities (inhomogeneity and anisotropy) were pointed out in Ref. 3, the attention was concentrated on the anisotropic case. This was not accidental. An inhomogeneous superconductor considered there was a bimetallic plate consisting of two soldered superconductors (Fig. 5). In this case an alloy may form along the interface (junction). At that time (in 1953) the alloys were regarded as somewhat "dirty" and it was held that studies of the superconductivity should be made using the "purest" possible materials (single crystals with the minimum concentrations of impurities and defects). Undoubtedly, this view has some justification, but nowadays the alloys in general and, more specifically, an inhomogeneous superconducting circuit can in no way be regarded as second-rate.

However, we shall consider first the anisotropy of a superconductor in the geometry shown in Fig. 6. Here, x' and z' are the symmetry axes of the crystal and $y' = y$ is also a symmetry axis. A temperature gradient ∇T is directed along the z axis, which is tilted at an angle φ to the z' axis. The solution of the problem is given in Ref. 4 and in the literature cited there. The result is as follows: a certain superconducting current I_s flows in a sample and its density $\mathbf{j}_s$ is significant only near the surface in a layer of thickness of the order of the depth of penetration δ of the magnetic field. The current I_s flowing around the sample creates a magnetic field $\mathbf{H}_T$, which is homogeneous across the thickness of the sample, directed along the y axis, and equal to

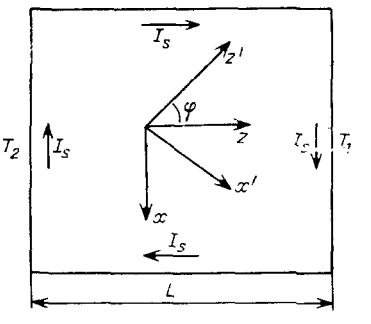

FIG. 6. Anisotropic (single-crystal) superconductor. The resultant superconducting current I_s creates a magnetic field $\mathbf{H}_T$, directed along the y axis.

$$H_T = \frac{4\pi}{c}\,\delta_0^2\,\frac{\alpha_{xx}b_{n,xz} + \alpha_{xz}b_{n,zz}}{T_c[1-(T/T_c)]^2}\left(\frac{dT}{dz}\right)^2$$

$$= \frac{2\pi}{c}\,\frac{\delta_0^2(\alpha_{z'}b_{z'} - \alpha_{x'}b_{x'})\sin 2\varphi}{T_c[1-(T/T_c)]^2}\left(\frac{dT}{dz}\right)^2, \qquad (22)$$

where $\alpha_{x'}$, $\alpha_{z'}$, $b_{x'}$, $b_{z'}$ represent, respectively, the principal values of the tensors α_{ik} and $b_{n,ik}$ corresponding to the symmetry axes x' and z'. We also have here

$$\Lambda_{ik} = \Lambda_0\alpha_{ik}, \quad \Lambda_0 = \frac{4\pi\delta^2}{c^2} = \frac{m}{e^2 n_s},$$
$$\delta^2 = \delta_0^2\left(1 - \frac{T}{T_c}\right)^{-1}, \qquad (23)$$

in the temperature interval close to T_c.

For example, in the case of tin we have $\delta_0 = 2.5\times 10^{-6}$ cm, $T_c = 3.72$ K, and if $(\alpha_{z'}b_{z'} - \alpha_{x'}b_{z'})\sin 2\varphi \sim b(T_c) \sim 10^{11} - 10^{12}$ cgs esu, we obtain

$$H_T \sim \frac{10^9 - 10^{10}}{[1-(T/T_c)]^2}\left(\frac{dT}{dz}\right)^2. \qquad (24)$$

If $1-(T/T_c)\sim 10^{-2}$ and $dT/dz = (T_2 - T_1)/L \sim 0.1$ K/cm, then the magnetic field is $H_T \sim 10^{-7}$–10^{-8} Oe. Such a field can be measured quite easily by modern methods, but because of a number of complications a comparison of the theory with experiment is not simple. Unfortunately, suitable measurements have been carried out only once quite a long time ago.[30] Some comments about that paper and the possibility of determination of H_T or of the field-originating current I_s were made in Ref. 4. To the best of my knowledge, after the appearance of the review of Ref. 4, only one relevant paper[31] was published and it deals with the theory of the thermoelectric effect in anisotropic superconductors. However, the problem deserves both experimental and theoretical study.

6. We shall now consider inhomogeneous isotropic superconductors, but not a bimetallic plate (Fig. 5): instead we shall consider a totally superconducting circuit formed by two metals (Fig. 7). Obviously, the usual thermoelectric circuit of two conductors made of metals I and II is a special case of the circuit in Fig. 7. Naturally, a bimetallic plate can also be regarded as a limiting variant of the circuit in Fig. 7 in the absence of an open gap. However, the presence of an open gap in a massive circuit when its thickness d (for example, the diameter of the wire forming the circuit) is much greater than the depth of penetration δ of the field makes it possible to calculate readily the magnetic flux Φ across the gap without solving the problem completely.[32,33] With this in mind we shall assume that in the bulk of a superconductor we practically have $\mathbf{j} = \mathbf{j}_s + \mathbf{j}_n = 0$ (see above) i.e., we shall assume that

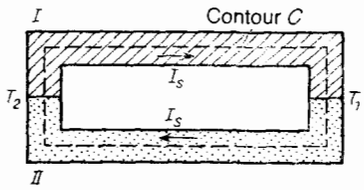

FIG. 7. Totally superconducting circuit made of two metals I and II. The contour C lies in the bulk of the semiconductors. The current I_s flows on the inner surface of the circuit (aperture) in a layer of thickness of the order of δ.

$$\mathbf{j}_n = b_n\nabla T = -\mathbf{j}_s = +\frac{ie\hbar}{2m}(\Psi^*\nabla\Psi - \Psi\nabla\Psi^*) + \frac{2e^2}{mc}\mathbf{A}\,|\Psi|^2$$
$$= -\frac{e\hbar n_s}{2m}\left(\nabla\varphi - \frac{2e}{\hbar c}\mathbf{A}\right), \qquad (25)$$

where the familiar expression for the superconducting current density[4] is used and the order parameter is expressed in the form $\Psi = (n_s/2)^{1/2}e^{i\varphi}$, where n_s is the density of the "superconducting" electrons (the density of pairs with a mass $2m$ and a charge $2e$ is $n_s/2$). We shall integrate Eq. (25) along the contour C, which is in the bulk of the superconductor and is represented by the dashed line in Fig. 7. We shall bear in mind that $\oint \mathbf{A}ds = \int \mathbf{H}dS = \Phi$ and $\int \nabla\varphi\, ds = 2\pi n$, where $n = 0, 1, 2, \ldots$ (obviously, $\mathbf{H} = \mathrm{curl}\,\mathbf{A}$, where $\mathbf{A}$ is the vector potential). We then obtain directly

$$\Phi = n\Phi_0 + \int_{T_1}^{T_2}(b_{n,II}\delta_{II}^2 - b_{n,I}\delta_I^2)\,dT; \qquad (26)$$

where $m/e^2n_s = \Lambda_0 = 4\pi\delta^2/c^2$, δ is the depth of penetration of a field, and $\Phi_0 = \pi\hbar c/e = hc/2e = 2\cdot 10^{-7}$ Oe·cm^2 is a quantum of the magnetic flux. The relationship (26) can be readily obtained for $n = 0$ from the London–London equation without introducing Ψ. We can do this also for $n \neq 0$, but subject to an additional assumption such as the Bohr quantization condition (see Ref. 4). The current I_s, which leads to the appearance of a flux Φ, flows on the internal surface of the circuit (ring, etc.) in a layer of thickness of the order of δ; this applies also to a bimetallic plate: a field H_T appears at right-angles to the plane of the plate and the current I_s flows in the region of the junction again in a layer of thickness of the order of δ (Fig. 5). As pointed out already, the current I_s is very small compared with the current I_n, which appears in a similar normal circuit. Therefore, in the usual measurements of the thermoelectric current the contribution I_s cannot be detected. The nature of the current I_s makes it superconducting (it does not carry heat) and it is established in the process of formation of a temperature gradient in the circuit (for details see Ref. 4).

If, for the sake of simplicity, we assume that $(b_n\delta^2)_{II} \gg (b_n\delta^2)_I$ and $\delta_{II}^2 = \delta_{0,II}^2[1-(T/T_c)]^{-1}$, we then find from Eq. (26) that

$$\Phi_T = \Phi - n\Phi_0 \approx \frac{4\pi}{c}\,b_{n,II}\delta_{0,II}^2 T_c \ln\frac{T_c - T_1}{T_c - T_2}. \qquad (27)$$

In the case of high-quality samples of tin, we have $b(T_c)\sim 10^{11}$–10^{12} cgs esu, $\delta_0 \approx 2.5\times 10^{-6}$ cm, and for $T_0 - T_2 \sim 10^{-2}$ K and $T_c - T_1 \sim 0.1$ K, and generally for $\ln[(T_c - T_1)/(T_c - T_2)] \sim 1$, the flux is $\Phi_c \sim 10^{-2}\Phi_0$, i.e., in principle, it can be detected quite readily by modern methods.

The flux Φ_T was measured in several investigations mentioned in the reviews,[4,5] but I am not aware of any reports of new experiments after 1982, which is the reason I am referring only to the reviews.[4,5] In the case of open circuits (of the wire ring type) the experiments are in agreement with theory [we are speaking here of Eq. (27)]. However, in the case of a circuit of the toroidal type[5] with a closed magnetic flux the observed values of Φ_T are considerably higher than the values predicted by Eq. (27) and have a different temperature dependence. On the whole, the experimental side of this topic is still an unsolved problem. The discrepan-

cies between the theory presented above and the experiments can be explained in a variety of ways mentioned already in Refs. 4, 5, and 34–36. For example, it is suggested in Refs. 34 and 35 that heating of the circuit results in the trapping of an increasing flux, i.e., the number of the flux quanta n in Eq. (26) is a function of the temperature T of a sample and may be large. However, the total flux $\Phi = n(T)\Phi_0 + \Phi_T$ is measured. The high experimental value of Φ is attributed in Ref. 36 to surface and contact effects. It would seem that these hypotheses could be checked by changing first of all the geometry of the circuit. In particular, the role of the trapped flux $n\Phi_0$ can quite readily be identified at least qualitatively by considering a bimetallic plate (Fig. 5) for which there is no aperture at all and, therefore, we always have $n = 0$. One should stress also the importance of theoretical and experimental investigations of contacts, of the regions close to them, and of the ends of an open circuit, particularly the ends of a rod shown schematically in Fig. 3. At these ends the current $\mathbf{j}_s$ is converted into $\mathbf{j}_n$ and vice versa. How does it occur in detail?

7. We must stress that the thermoelectric effects in the superconducting state are not limited to those discussed above: there are also other effects or their variants (see Refs. 3, 5, and 37–39 and the literature cited there). Since I have not analyzed these effects and in view of the nature of the present paper, mentioned at the beginning, I shall stop here,[2)] but with one exception. The enormous interest in high-temperature superconductors suggests that the specific properties of these materials should be considered from the point of view of observation of the thermoelectric effects. Possibly the most important feature of high-temperature superconductors from this point of view was mentioned above: it is the circular thermal conductivity (Secs. 3 and 4). Since the majority of the known high-temperature superconductors are strongly anisotropic, they are suitable thus for the observation of thermoelectric generation of a magnetic field in a crystal (Sec. 5). One can investigate also circuits composed entirely of high-temperature superconductors or containing them. If in the case of high-temperature superconductors we use the published values of $S(T_c)$ and $\sigma(T_c)$ and regard them as typical also in the superconducting state near T_c, then $S \sim 10^{-5}$ V/K, $\sigma = 1/\rho \sim 10^3\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$, and hence $b = \sigma S \sim 10^{-2}\ \mathrm{V}\cdot\Omega^{-1}\cdot\mathrm{cm}^{-1}\cdot\mathrm{K}^{-1}$. On the other hand, the case of—for example—tin,[4] we have $\sigma \sim 10^9\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$, $S \sim 10^{-7}$ V/K and $b \sim 10^2\ \mathrm{V}\cdot\Omega^{-1}\cdot\mathrm{cm}^{-1}\cdot\mathrm{K}^{-1}$. Since the magnetic field flux in the thermoelectric circuit and the field in an anisotropic superconductor are proportional to $b_n\delta^2$ [see Eqs. (26) and (22)], the smallness of the coefficient b_n in ceramic high-temperature superconductors (compared with ordinary superconductors) will reduce the effects under consideration, even in spite of the somewhat higher values of δ. However, we do not know what are the true values of b_n for high-temperature superconductor crystals at temperatures $T < T_s$. They may not be that small for the s-pairing case and in the exotic pairing situation they may be considerable.[19,20] This makes such measurements even more desirable.

Finally, a specific feature of high-temperature superconductors is the short coherence length ξ_0. Consequently, fluctuations near T_c are strong in high-temperature superconductors (these fluctuations are proportional to ξ_0^{-6}—see Ref. 41). Therefore, the fluctuation corrections for the thermoelectric effect near T_c are also large. Moreover, such fluctuations have indeed been observed at temperatures $T > T_c$ (Ref. 17); a theoretical paper on this topic has appeared.[42] Fluctuations should occur also below T_c, but in this case they naturally cannot be observed in the usual way by measuring S. An investigation of fluctuations of the thermoelectric effects in high-temperature superconductors both at $T > T_c$ and $T < T_c$ deserves serious attention. This applies, as I tried to demonstrate, to the whole problem of the thermoelectric effects in the superconducting state.

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1) It should be stressed that the homogeneity, i.e., independence of the properties of the coordinates, is understood to be the homogeneity when $\nabla T = 0$.

2) It is interesting to note that in the case of a closed multiply connected container ("circuit") filled with He II (or, in principle, with some other superfluid liquid), we should observe, and this has been confirmed, a characteristic thermomechanical circulation effect,[40] which is somewhat analogous to the thermoelectric current in a closed superconducting circuit (Fig. 7).

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