Theory of a large thermoeffect in superconductors doped with magnetic impurities

Mikhail S. Kalenkov,1, 2 Andrei D. Zaikin,3, 1, 2 and Leonid S. Kuzmin4, 2

1I.E. Tamm Department of Theoretical Physics, P.N. Lebedev Physical Institute, 119991 Moscow, Russia
2Laboratory of Cryogenic Nanoelectronics, Nizhny Novgorod State Technical University, 603950 Nizhny Novgorod, Russia
3Institut für Nanotechnologie, Karlsruher Institut für Technologie (KIT), 76021 Karlsruhe, Germany
4Chalmers University of Technology, Gothenburg, Sweden

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Application of an electric field \( E \) to a normal conductor with Drude conductivity \( \sigma_N \) yields an electric current \( j = \sigma_N E \) across this conductor. A similar effect can be produced by a temperature gradient \( \nabla T \). In this case the current \( j \) induced in a sample takes the form \( j = \alpha N \nabla T \), where \( \alpha_N \sim (\sigma_N/e)(T/\epsilon_F) \) is thermoelectric coefficient and \( \epsilon_F \) is the Fermi energy. The latter simple equations illustrate the essence of the so-called thermoelectric effect in normal metals.

If a metal becomes superconducting, the situation changes significantly. On one hand, the electric field cannot anymore penetrate into a superconductor and, hence, the Drude contribution to the current is absent in this case. On the other hand, a supercurrent \( j_s \) can now be induced in the sample without any electric field. It follows immediately that by applying a temperature gradient to a uniform superconductor one would not be able to induce any current since thermal current would be exactly compensated by the supercurrent \( j_s = -\alpha \nabla T \), where \( \alpha \) defines thermoelectric coefficient in a superconducting state. Ginzburg [1, 2] demonstrated that no such compensation generally occurs in non-uniform superconductors which opens a possibility to experimentally detect thermoelectric current in such structures. Several experiments with bimetallic superconducting rings (see Fig. 1) have been performed [3–5] which indeed revealed the presence of thermoelectric magnetic flux in such rings. However, both the magnitude of the effect and its temperature dependence turned out to be in a strong disagreement with available theoretical predictions [6]. Quite surprisingly, the magnitude of the thermoeffect detected in these experiments exceeded theoretical estimates by several orders of magnitude. Subsequently, a good agreement between theory and experiment [6] was claimed, but this report remained largely unnoticed. In any case, no convincing explanation of the discrepancy between experiments [3–5] and theory [6] was offered and the paradox remains unresolved until now [8].

In this Letter we are not aiming at directly resolving this long standing paradox. Rather our primary goal is to identify the conditions under which thermoelectric currents in superconductors can be significantly enhanced. In the normal state contributions to the thermoelectric coefficient \( \alpha_N \) from electron-like and hole-like excitations are of the opposite sign and almost cancel each other. A similar situation occurs in conventional superconductors where the thermoelectric coefficient \( \alpha \) also remains small [7] and monotonously decreases with \( T \) below the critical temperature \( T_c \). On the other hand, in unconventional superconductors impurity scattering may lead to much larger values of \( \alpha \) due to formation of quasi-bound Andreev bound states near impurities which yield high asymmetry between electron and hole scattering rates [3, 10].

Here we will demonstrate that “giant” thermoeffect can also be expected in conventional superconductors doped by magnetic impurities. Also in this case Andreev bound states are formed near such impurities [11, 12] thereby explicitly breaking the symmetry between electron and holes [14, 15]. We argue that this feature may cause parametrically strong enhancement of the thermoeffect in such systems

\[
\alpha/\alpha_N(T_c) \sim p_F \ell \gg 1,
\]

where \( p_F = m\nu_F \) is the Fermi momentum and \( \ell \) is the electron elastic mean free path in the absence of magnetic impurities. This formula remains valid in the most relevant diffusive limit \( \ell \lesssim \nu_F/T_c \) and at an “optimal” concentration of magnetic impurities \( n_{\text{imp}} \) roughly equal.
to one half of the critical one (see below). Eq. (11) predicts possible enhancement of the thermoeffect in superconductors with magnetic impurities by several orders of magnitude as compared to that in the normal state at $T = T_c$.

Quasiclassical formalism and impurity self-averaging. In what follows we will consider a superconductor which contains both non-magnetic and magnetic impurities. Our analysis is based on the quasiclassical formalism of nonequilibrium Green-Keldysh matrix functions $\hat{g}$ obeying the Eilenberger equations [16]. Unfortunately this approximation is insufficient for isotropic impurities while the second term $\hat{\Sigma}$ is localized near each magnetic impurity in a superconductor [11, 12]. Similarly to the case of unconventional superconductors with non-magnetic impurities [3, 11] these Andreev bound states yield different scattering rates for electrons and holes and, hence, break the electron-hole symmetry in our system thereby causing strong enhancement of the thermoeffect.

Consider the retarded part of the self-energy $\hat{\Sigma}$ [3]. It can be written in the form

$$\hat{\Sigma}^R = \left( \begin{array}{cc} \Sigma^R_{++} - \Sigma^R_{--} & \Sigma^R_{+-} + \Sigma^R_{-+} \\ \Sigma^R_{-+} - \Sigma^R_{++} & \Sigma^R_{--} + \Sigma^R_{+-} \end{array} \right),$$

where non-vanishing diagonal part $\Sigma^R_{++}$ explicitly accounts for asymmetry between electrons and holes [13]. Substituting the retarded Green function matrix

$$\hat{g}^R = \frac{1}{\sqrt{\varepsilon^2 - \Delta^2}} \left( \begin{array}{cc} \varepsilon & \Delta \\ -\Delta & -\varepsilon \end{array} \right)$$

into Eqs. (6), (9) we evaluate $\hat{\Sigma}^R$ as well as the energy resolved superconducting density of states $\nu(\varepsilon)$ normalized to its normal state value. Introducing the parameter $\varepsilon = \tilde{\varepsilon}/\Delta$ we get

$$\Sigma^R_0(\varepsilon) = \frac{\varepsilon^2 - \Delta^2}{\varepsilon^2 - \beta^2 \Delta^2}, \quad \nu(\varepsilon) = \text{Re} \frac{\varepsilon}{\sqrt{\varepsilon^2 - \Delta^2}}.$$}

The scattering parameters $\Gamma_{0,1,2}$ have the dimension of rates being proportional to the concentration of magnetic impurities $n_{\text{imp}}$. They read

$$\Gamma_0 = \frac{n_{\text{imp}}}{\pi N_0} \frac{u_1 (1 + u_2^2 - u_2^2)}{(1 + u_1^2 - u_2^2)^2 + 4u_2^2},$$

$$\Gamma_1 = \frac{n_{\text{imp}}}{\pi N_0} \frac{(1 + u_1^2 - u_2^2)(u_2^2 - u_2^2)}{(1 + u_1^2 - u_2^2)^2 + 4u_2^2},$$

$$\Gamma_2 = \frac{2n_{\text{imp}}}{\pi N_0} \frac{u_2^2}{(1 + u_1^2 - u_2^2)^2 + 4u_2^2}.$$
pair-breaking effect in bulk conventional superconductors. On the contrary, scattering on magnetic impurities may strongly modify these parameters. For illustration, the density of states $\nu(\varepsilon)$ is depicted in Fig. 2 at $\varepsilon > 0$ and different values $n_{imp}$. With increasing $n_{imp}$ Andreev levels get broadened forming two impurity bands respectively at positive and negative energies. Further increase of $n_{imp}$ yields even broader bands which eventually merge with continuum (overgap) states.

Thermoeffect enhancement by magnetic impurities. We are now prepared to evaluate the thermoelectric coefficient $\alpha$. In doing so we will essentially follow the quasiclassical linear response theory initially formulated in Ref. 18 for the analysis of thermal conductivity in unconventional superconductors. This approach allows to recover the dominating contribution to the thermoelectric coefficient $\alpha$ which originates from the electron-hole asymmetry. Employing Eqs. (2) and proceeding along the lines with Ref. 18 we evaluate the correction to the Keldysh Green function $\delta g^K \propto v_F \nabla T$ [19]. Combining the resulting expression with Eq. (7) we obtain

$$\alpha = -\frac{eN_0v_F^2}{12T^2} \int_{-\infty}^{\infty} \frac{\mathcal{F}(\varepsilon) d\varepsilon}{\cosh^2(\varepsilon/2T)},$$

(17)

$$\mathcal{F}(\varepsilon) = \frac{\nu(\varepsilon) \text{Im} \Sigma_{R}(\varepsilon)}{[\text{Re} \sqrt{\Delta^2 - \varepsilon^2}] - [\text{Im} \Sigma_{R}(\varepsilon)]^2}.$$  

(18)

Eqs. (17)-(18) — together with Eqs. (11)-(16) — constitute the central result of this work which accounts for “giant” thermoeffect in superconductors doped by magnetic impurities. In the most relevant case of diffusive superconductors with $\Gamma \gtrsim T_c$, Eq. (18) reduces to $\mathcal{F}(\varepsilon) = \nu(\varepsilon) \text{Im} \Sigma_{R}(\varepsilon)/\Gamma T^2$, i.e. $\alpha \propto 1/\Gamma^2$ in this limit.

At small magnetic impurity concentrations $\Gamma_2 \ll \Delta$ the impurity band is restricted to subgap energies $\varepsilon < \Delta$, cf. Fig. 2. At energies within the impurity band one has

$$\mathcal{F}(\varepsilon) = \frac{\Gamma_0 [2\Gamma_2 \Delta \sqrt{1 - \beta^2} - (|\varepsilon| - \beta \Delta)]}{4\Gamma_2 (1 - \beta^2)(\Delta \sqrt{1 - \beta^2} + \Gamma)^2}.$$  

(19)

Substituting this expression into Eq. (17), integrating over all impurity band energies and taking the limit $\Gamma_2 \ll \Delta, T^2/\Delta$, we arrive at the subgap contribution to $\alpha$:

$$\alpha_{sg} = -\frac{eN_0v_F^2}{9T^2} \left(\frac{1}{(1 - \beta^2)^{1/4}} \Delta \sqrt{1 - \beta^2 + \Gamma} \Delta^{3/2} \right),$$

(20)

i.e. $\alpha_{sg} \propto n_{imp}^{3/2}$ at small concentrations of magnetic impurities. Assuming that the impurity band is located at $\varepsilon \sim \Delta/2$ ($\beta \sim 0.5$) and setting $T \sim \Delta \sim \Gamma_{0,1,2}$ we get

$$\alpha_{sg} = -eN_0v_F^2T/\Gamma^2 \sim \alpha_{og}p_F\ell.$$  

(21)

This estimate demonstrates that $\alpha_{sg}$ may strongly exceed the thermoelectric coefficient in the normal state.

Additional contribution to $\alpha$ is provided by overgap energies. For small values $n_{imp}$ we can use the standard BCS expression for the density of states and derive

$$\mathcal{F}(\varepsilon) = \frac{2\Gamma_0 \Gamma_2 (1 - \beta^2)e^{4\Delta^2}[\varepsilon^2 - \beta^2 \Delta^2]^{-1}}{[\Gamma_2 \varepsilon^2 + \Gamma_1 (\varepsilon^2 - \beta^2 \Delta^2) + \Gamma_4 (\varepsilon^2 - \Delta^2)]^2}.$$  

(22)

Combining Eqs. (22) and (17), in a realistic limit $\Gamma \gg \Gamma_{1,2}$ and for $T \sim \Delta$ we recover the contribution to $\alpha$ from overgap energies

$$\alpha_{og} \sim -eN_0v_F^2 \frac{\Gamma_0 \Gamma_2}{\Delta^2} \sim \alpha\nu p_F \ell.$$  

(23)

In the optimal case $T \sim \Delta \sim \Gamma_{0,1,2}$, we find $\alpha_{og} \sim \alpha_{sg}$, where the latter quantity obeys Eq. (21). Hence, also for $\alpha = \alpha_{sg} + \alpha_{og}$ we recover the estimate (1).

At temperatures close to $T_c$ the value $\alpha$ can be evaluated analytically at any concentration of impurities. In this limit one can set $\nu(\varepsilon) = 1$ and obtain

$$\mathcal{F}(\varepsilon) = \frac{2\Gamma_0 \Gamma_2 (1 - \beta^2)e^{4\Delta^2}}{(\varepsilon^2 + \Gamma_2^2)\Delta^2(\Gamma + \Gamma_1 + \Gamma_2)^2}.$$  

(24)
which yields
\[ \alpha = \frac{e N_0 v_F^2}{6 \pi T^2} \frac{\Gamma_0 (1 - \beta^2) \Delta^2}{(\Gamma_1 + \Gamma_2)^2} S \left( \frac{\Gamma_2}{2 \pi T} \right), \quad (25) \]
where \( S(x) = [x \psi'(x + 1/2)]' \) and \( \psi(x) \) is the digamma function.

The results of numerical evaluation of \( \alpha \) as a function of both temperature and impurity concentration are displayed in Fig. 3. We observe that the thermoelectric coefficient of a diffusive superconductor achieves its maximum value at temperatures \( T \sim T_c/2 \) and \( n_{\text{imp}} \) approximately equal to one-half of the critical concentration at which superconductivity gets fully suppressed. This maximum value can be estimated as
\[ \max_{T, n_{\text{imp}}} |\alpha| \approx 0.05 \frac{e N_0 v_F^2 T_{c0}}{\Gamma^2} = 0.2 \epsilon N_0 T_{c0} \ell^2. \quad (26) \]

Combining the expression for \( \alpha_N \sim (\sigma_N/e)(T/\epsilon_F) \) with Eq. (26) we arrive at the estimate (11) which demonstrates that enhancement of the thermoeffect is stronger in cleaner superconductors. At the borderline of applicability of Eq. (11) \( \ell \sim v_F/T_c \) we obtain \( |\alpha| \sim \sigma_N/e \), which appears to define the absolute maximum value of \( \alpha \) in conventional superconductors doped by magnetic impurities.

It is interesting to point out that the presence of electron-hole asymmetry in such superconductors was also predicted to yield anomalously large photovoltaic effect [15]. Despite clear similarity between the models the effect [15] is substantially different from one analyzed here. Indeed, while no voltage occurs in the system within the linear response to a temperature gradient [19], a non-zero nonequilibrium voltage is induced as a second order response to an external electromagnetic field [15]. Hence, thermal heating of the system considered here is physically not equivalent to that produced by an external ac field.

**Bimetallic superconducting rings and TEB.** Finally let us briefly discuss the possibility to experimentally detect “giant” thermoeffect predicted here. One way to do so would be to perform an experiment with bimetallic superconducting rings [3-5] as shown in Fig. 1. Provided superconducting contacts are kept at different temperatures \( T_a \) and \( T_b \), thermoelectric current will be induced inside the ring and the corresponding magnetic flux \( \Phi \) can be measured. The magnitude of this flux reads
\[ \frac{\Phi}{\Phi_0} = \frac{4e}{c^2} \int_{T_a}^{T_b} [\lambda_1^2(T)\alpha_1(T) - \lambda_2^2(T)\alpha_2(T)] dT, \quad (27) \]

where \( \Phi_0 = \pi c/e \) is flux quantum, \( \alpha_{1,2} \) and \( \lambda_{1,2} \) define respectively thermoelectric coefficients and the values of London penetration depth for two superconductors. For simplicity we may assume \( \alpha_1 \gg \alpha_2 \) and neglect the second term in Eq. (27). Employing Eq. (26) together with the standard expression for the London penetration depth in diffusive superconductors at \( T = 0 \) we arrive at a conservative estimate for the thermally induced flux
\[ \frac{|\Phi|}{\Phi_0} \sim 0.01 \frac{T_b - T_a}{\Gamma}, \quad \Gamma \gtrsim T_{c0}. \quad (28) \]

In Fig. 4 we display the temperature dependence of the combination \( \lambda^2(T)/\alpha(T) \) at different concentrations of magnetic impurities. Induced thermoﬂux \( \Phi \) (normalized to \( \Phi_0 \)) equals to the area under the corresponding curve between \( T_a \) and \( T_b \). For reasonably clean superconductors typical values of \( \Phi \) may easily reach \( \Phi \gtrsim 10^{-2}\Phi_0 \). Another way to experimentally test our predictions would be to employ a novel type of zero-biased thermoelectric bolometer (TEB) [20]. This TEB consists of a superconducting absorber attached to normal and superconducting electrodes via tunnel junctions (SIN and SIS' junctions). Incoming photons excite quasiparticles in the absorber. Strong charge imbalance between excited quasiparticles and quasiholes can be expected provided this absorber is formed by a superconductor doped by magnetic impurities. Temperature gradient across the superconductor will occur due to permanent escape of excited quasiparticles from the “cold” end of the absorber through SIN junction, whereas no such escape would be possible in its “hot” end attached to SIS' junction. As a result, permanent thermoelectric current will flow in the absorber creating “giant” thermoelectric voltage response which can be detected experimentally.

In summary, we have demonstrated that “giant” thermoeffect might occur in conventional superconductors doped by magnetic impurities. This effect is well in the measurable range and can be detected in modern experiments.

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