Thermoelectric effect in superconductors with nonmagnetic localized states

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The thermoelectric effect is investigated in superconductors containing a nonmagnetic impurity with a localized state near the Fermi surface. It is shown that at $T \lesssim T_c$ the coefficient η, which characterizes this effect, is larger than in the normal state. For temperatures close to T_c this leads to a severalfold increase of the thermoelectric angle.

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Much attention is being paid recently to the study of the thermoelectric effect in superconductors.[1–3] The purpose of the present study is to investigate this effect in a metal containing a nonmagnetic impurity with a localized level near the Fermi surface.[4] Resonant scattering of electrons by such impurities influences significantly the properties of both normal metals and superconductors.[5–8] This is particularly manifest in the thermoelectric effect, because the relaxation time in resonant scattering is odd in the energy, and this leads to a nonzero differential thermoelectric power in the zeroth order in T/μ (μ is the chemical potential of the system).[5,9]

A temperature gradient produces in a superconductor a normal-excitation current[10]:

$$j^T = -\eta_s \nabla T. \tag{1}$$

To calculate the coefficient η_s which characterizes this current, we start from the formula[11]:

$$\eta_s = -\frac{1}{3T}\lim_{\omega\to 0}\operatorname{Im}\frac{P(q=0,\omega)}{\omega}, \tag{2}$$

where $P(q, \omega)$ is the Fourier component of the retarded Green's function $\langle\langle j(x,0) j^H(x't)\rangle\rangle$.

After averaging over the positions of the impurity atoms, we obtain for P the expression

$$P(q=0,\nu_m) = \frac{e}{m^2}\frac{1}{\beta}\sum_{\omega_n}(2\omega_n-\nu_m)\int\frac{d^3k}{(2\pi)^3}k^2\mathcal{P}_{11}(k\omega_n\omega_n-\nu_m), \tag{3}$$

$$\nu_m = 2\pi m i/\beta,\quad \omega_n=(2n+1)\pi i/\beta,\quad \beta=(k_bT)^{-1},$$

$$\mathcal{P}(k\omega_n\omega_n-\nu_m) = (\tau_3\times 1)G(k\omega_n)(\tau_3\times 1)G(k\omega_n-\nu_m), \tag{4}$$

where $G(k\omega_n)$ is the single-particle Green's function averaged over the impurity. It is given in[7,8]. In the derivation of (3) we assume the scattering to be isotropic, and therefore the average of the products of two Green's functions has been replaced by the product of the averages.

After integrating with respect to the energy $\xi(\xi=\varepsilon-\mu)$ and carrying out an analytic continuation ($\nu_m \to z$)[12] we obtain for η_s

$$\eta_s = \frac{e}{6T}\int_{-\infty}^{\infty}dz\,z\frac{\partial f}{\partial z}\frac{N(\mu+z)v^2(\mu+z)}{\operatorname{Im}\varepsilon_1(z)\operatorname{Im}\varepsilon_2(z)}\Big[\operatorname{Im}(\tilde{Z}^2(z)-\tilde{\Delta}^2(z))^{1/2}\Big(1+\frac{|u|^2-1}{|u^2-1|}\Big)$$

$$-2\operatorname{Im}\chi(z)\operatorname{Re}\frac{\tilde{Z}(z)}{(\tilde{Z}^2(z)-\tilde{\Delta}^2(z))^{1/2}}\Big], \tag{5}$$

$$f(z)=(1+\exp\beta z)^{-1},$$

$$\varepsilon_{1,2} = \pm(\tilde{Z}^2(z)-\tilde{\Delta}^2(z))^{1/2}+\chi(z),\quad u=\tilde{Z}(z)/\tilde{\Delta}(z), \tag{6}$$

$$\tilde{Z}(z) = z+\frac{n_{imp}\Gamma}{\pi N(\mu+z)}\Big(z+\frac{u\Gamma}{(1-u^2)^{1/2}}\Big)A^{-1}, \tag{7}$$

$$\tilde{\Delta}(z) = \Delta+\frac{n_{imp}\Gamma}{\pi N(\mu+z)}\Big(\Delta_d+\frac{\Gamma}{(1-u^2)^{1/2}}\Big)A^{-1}, \tag{8}$$

$$\chi(z) = \frac{n_{imp}}{\pi N(\mu+z)}\Gamma\varepsilon_d A^{-1}, \tag{9}$$

$$A = \varepsilon_d^2+\Gamma^2-z^2+\Delta^2d^2-\frac{2\Gamma\Delta}{(1-u^2)^{1/2}}\Big(u\frac{z}{\Delta}+d\Big), \tag{10}$$

n_{imp} is the concentration of the impurity atoms, $N(\varepsilon)$ is the state density of the electrons in the normal metal, $v=|\partial\varepsilon/\partial p|$, Γ is the width of the level of the impurity atom, the energy ε_d of the level of the impurity atom is reckoned from the Fermi surface, $d=-\Delta_d/\Delta$, and the quantity Δ_d characterizes the influence of the Coulomb repulsion of the impurity-atom electrons with opposite spins on the superconducting properties.[7]

Taking into account the analytic properties of the functions $\tilde{Z}(z)$, $\tilde{\Delta}(z)$, $\chi(z)$ and $u(z)$ and expanding the smooth quantities near the Fermi surface, we obtain

$$\eta_s = \eta_{s1}+\eta_{s2}; \tag{11}$$

$$\eta_{s1} = \frac{e}{12T^2}\frac{d}{d\varepsilon}\Big[\frac{\operatorname{Im}(\tilde{Z}^2(\varepsilon)-\tilde{\Delta}^2(\varepsilon))^{1/2}}{\operatorname{Im}\varepsilon_1(\varepsilon)\operatorname{Im}\varepsilon_2(\varepsilon)}N(\varepsilon)v^2(\varepsilon)\Big]\Big|_{\varepsilon=\mu}$$

$$\int_0^{\infty}\frac{dz\,z^2}{\operatorname{ch}^2(\beta z/2)}\Big(1+\frac{|u|^2-1}{|u^2-1|}\Big), \tag{12}$$

$$\eta_{s2} = \frac{e}{6T^2}N(\mu)v^2(\mu)\int_0^{\infty}\frac{z\,dz}{\operatorname{ch}^2(\beta z/2)}\frac{n(z)\operatorname{Im}\chi(z)}{\operatorname{Im}\varepsilon_1(z)\operatorname{Im}\varepsilon_2(z)}, \tag{13}$$

$$n(z) = \operatorname{Re}\frac{u(z)}{(u^2(z)-1)^{1/2}}. \tag{14}$$

The integrals in (12) and (13) are calculated on the basis of the method developed by Moskalenko *et al.*[13] In this case the small parameter is the quantity $\sigma=\alpha\lambda$, where

$$\alpha = 2\Gamma\Delta(\varepsilon_d^2+\Gamma^2)^{-1},\ \lambda=c(1+d)^2(1+c)^{-2}(1-dc)^{-1},$$
$$c=n_{imp}\Gamma[\pi N(\mu)(\varepsilon_d^2+\Gamma^2)]^{-1}\quad (\text{see }[8]).$$

Expanding in terms of this small parameter, we obtain

$$\operatorname{Im}(\tilde{Z}^2(z)-\tilde{\Delta}^2(z))^{1/2}\sim c\Gamma,\quad \operatorname{Im}\varepsilon_{1,2}\sim\pm c\Gamma$$

in the entire frequency range. This has made it possible, when writing down formulas (12), to regard the functions $\mathrm{Im}(\tilde{Z}^2(z)-\tilde{\Delta}^2(z))^{1/2}$ and $\mathrm{Im}\,\varepsilon_{1,2}$ as smoothly varying in the energy. As to the function $\mathrm{Im}\chi(z)$, it is proportional to the state density, and therefore its values are different near the energy gap ω_g and far from it.

For the frequencies from ω_g to ω_c (ω_c is the frequency at which the quantities become continuous,[13] we have[8]

$$n(z)=n_0(x)/\sigma^{1/3},\qquad \mathrm{Im}\,\chi(z)=\frac{c\varepsilon_d\alpha^{1/3}(1+d)}{(1+c)\lambda^{1/3}}n_0(x), \tag{15}$$

where

$$z(x)=\Delta_g(1-{}^3/_2\sigma^{2/3}x+\ldots),\quad n_0(x)={}^1/_4\sqrt{3}(v^2(x)-u^2(x)),$$
$$u(x)=(-1+\sqrt{1-x^3})^{1/3},\quad v(x)=(-1-\sqrt{1-x^3})^{1/3}.$$

In the region of frequencies from ω_c to ∞ we obtain[8]

$$n(z)=\frac{u_0}{(u_0^2-1)^{1/2}},\qquad \mathrm{Im}\,\chi(z)=\frac{c\varepsilon_d\alpha(zu_0/\Delta+d)}{(u_0^2-1)^{1/2}}, \tag{16}$$

$$u_0=z/\Delta_g,\quad \Delta_g=\Delta(1-dc)(1+c)^{-1}=\Delta f. \tag{17}$$

We calculate first η_{s1}. The integral in (12) coincides with the integral for the thermal-conductivity coefficient.[8] In the region of temperatures satisfying the inequality $\sigma^{2/3}\ll(\beta\Delta_g)^{-1}\ll 1$ we have

$$\eta_{s1}=\frac{eT}{6}\frac{d}{d\varepsilon}\left(\frac{N(\varepsilon)v^2(\varepsilon)}{c\Gamma}\right)\Big|_{\varepsilon=\mu}\left[\int_{\Delta_g\beta}^{\infty}\frac{y^2\,dy}{\mathrm{ch}^2\,{}^1/_2y}+\frac{9}{20}\frac{(\Delta_g\beta)^3\sigma^{2/3}}{\mathrm{ch}^2\,{}^1/_2\Delta_g\beta}\right]. \tag{18}$$

At temperatures close to T_c, when $\Delta(T)/T\ll(T/\Gamma)^3$, we obtain for η_{s1}

$$\eta_{s1}=\frac{eT}{6}\frac{d}{d\varepsilon}\left(\frac{N(\varepsilon)v^2(\varepsilon)}{c\Gamma}\right)\Big|_{\varepsilon=\mu}\left[\int_{\Delta_g\beta}^{\infty}\frac{y^2\,dy}{\mathrm{ch}^2\,{}^1/_2y}+\frac{T^2}{\varepsilon_d^2+\Gamma^2}\int_{\Delta_g\beta}^{\infty}\frac{y^4\,dy}{\mathrm{ch}^2\,{}^1/_2y}\right]. \tag{19}$$

It is seen from the last formulas that at $\Gamma\gg\Delta$ and $\Gamma/T\gg 1$ we are left only with the first term, and if we assume $c\Gamma=1/2\tau_{t2}$, then this term is equal to the coefficient η for superconductors in the case of elastic scattering of the electrons by the nonmagnetic-impurity atoms.[1]

To calculate η_{s2} we divide the integration region in (13) into two intervals, (ω_g,ω_c) and (ω_c,∞), and substitute expressions (15) and (16) for $\mathrm{Im}\chi(z)$ and $n(z)$, respectively. We then have

$$\eta_{s2}=\frac{e}{6T^2}\pi\frac{N^2(\mu)v^2(\mu)}{n_{\mathrm{imp}}}\left[\frac{3}{2}\frac{\Delta_g^2\sigma}{\mathrm{ch}^2\,{}^1/_2\Delta_g\beta}\frac{\varepsilon_d}{\Gamma^3}\frac{(\varepsilon_d^2+\Gamma^2)(1+c)}{c(1+d)}\right.$$
$$\left.\cdot(1-cd)\int_1^{x_c}n_0^2(x)\,dx-\frac{2\varepsilon_d}{\Gamma^2}T^3\int_{\omega_0\beta}^{\infty}\frac{(y^2-\Delta_g\Delta_d\beta^2)}{y^2-(\Delta_g\beta)^2}\frac{y^2\,dy}{\mathrm{ch}^2\,{}^1/_2y}\right], \tag{19'}$$

where x_c is determined from the relation[8,13] $\omega_g=\Delta_g(1-\frac{3}{2}\sigma^{2/3}x_c)$.

Separating in the last expression the principal contribution,[14] we obtain

$$\eta_{s2}=-\frac{eT\varepsilon_d}{3}\frac{N(\mu)v^2(\mu)}{c\Gamma(\varepsilon_d^2+\Gamma^2)}\left\{\int_{\Delta_g\beta}^{\infty}\frac{y^2\,dy}{\mathrm{ch}^2\,{}^1/_2y}+\frac{\Delta\beta(1+d)}{2(1+c)}\left[\frac{(\Delta_g\beta)^2}{\mathrm{ch}^2\,{}^1/_2\Delta_g\beta}\ln\frac{4}{3}\sigma^{-2/3}\right.\right.$$
$$\left.\left.-\int_{\Delta_g\beta}^{\infty}dy\frac{y(2-y\,\mathrm{th}\,{}^1/_2y)}{\mathrm{ch}^2\,{}^1/_2y}\ln\left(\frac{y-\Delta_g\beta}{y+\Delta_g\beta}\right)\right]\right\}. \tag{20}$$

At $\Delta=0$ we have

$$\eta_{s2}^n=-\frac{2}{9}\pi^2eT\varepsilon_d\frac{N(\mu)v^2(\mu)}{c\Gamma(\varepsilon_d^2+\Gamma^2)}. \tag{21}$$

Near T_c, when $\Delta_g\beta\ll 1$, we have

$$\frac{\eta_{s2}}{\eta_{s2}^n}=1-\frac{(\Delta_g\beta)^3}{2\pi^2}+\frac{3\Delta\beta(1+d)}{4\pi^2(1+c)}\left(\frac{(\Delta_g\beta)^2}{\mathrm{ch}^2\,{}^1/_2\Delta_g\beta}\ln\frac{4}{3}\sigma^{-2/3}+3\Delta_g\beta\right). \tag{22}$$

In the case of very low temperatures ($(\Delta_g\beta)^{-1}\ll\sigma^{2/3}\ll 1$) we can expand all the quantities near the energy gap. Then, starting from (13), we get

$$\frac{\eta_{s2}}{\eta_{s2}^n}=\frac{4}{\pi^2}\frac{\exp(-\Delta_g\beta)}{\sigma^{2/3}}\Delta\beta\frac{1+d}{1+c}. \tag{23}$$

Let us examine our results. If we assume that the quantites $N(\varepsilon)$, $v(\varepsilon)$, and $c\Gamma$ are proportional to $\sqrt{\varepsilon}$, then the ratio of the coefficients

$$\eta_{s2}^n,\quad \eta_{s1}^n=\frac{\pi^2}{9}eT\frac{d}{d\varepsilon}\left(\frac{N(\varepsilon)v^2(\varepsilon)}{c\Gamma}\right)\Big|_{\varepsilon=\mu}$$

is equal to $-\mu\varepsilon_d(\varepsilon_d^2+\Gamma^2)^{-1}$. On the other hand, the condition for the existence of a nonmagnetic alloy is of the form[4,7]

$$U\left[1+\frac{U}{\pi\varepsilon_d}\mathrm{arctg}\frac{\varepsilon_d}{\Gamma}\right]^{-1}\frac{\Gamma}{\pi(\Gamma^2+\varepsilon_d^2)}\ll 1. \tag{24}$$

At certain values of U (U is the Coulomb repulsion of the impurity-atom electrons having opposite spins) this condition can be satisfied at a ratio of ε_d to Γ. If $\Gamma\sim10^{-2}\mu$ and $\varepsilon_d\sim10^{-3}\mu$, then $\eta_{s2}^n/\eta_{s1}^n\sim 10$, and at $\Gamma\sim10^{-2}\mu$ and $\varepsilon_d\sim10^{-1}\mu$ we also have $\eta_{s2}^n/\eta_{s1}^n\sim 10$. In such alloys, too, the observed thermoelectric power is connected not with the weak dependence of the quantities $N(\varepsilon)$, $v(\varepsilon)$, and $c\Gamma$ on the energy near the Fermi surface, but with the fact that the relaxation time of the relaxation time of the resonant scattering of the electrons by the impurity atoms is odd in the energy.[9,15] This, just as in the case of the electron-phonon relaxation mechanism in the presence of an undamped current in a closed circuit of superconductors,[16] leads to a nonzero result for the thermoelectric power even in the zeroth order in T/μ.

Interest attaches also to the temperature dependence of the thermoelectric coefficient below the transition point. For temperatures T close to T_c, as seen from (22), the value of η_{s2} is larger in the superconducting state than in the normal state, this being due to the increase of the electron density of states $n(z)$ at $T<T_c$ near the energy gap. At low temperatures $T\ll T_c$, to the contrary, owing to the abrupt decrease of the number of normal excitations, the coefficient η_{s2} becomes exponentially small (formula (23)), i.e., the plot of η_{s2} against temperature goes through a maximum at $T<T_c$. This is similar to the temperature dependence of the nuclear spin relaxation rate in the superconducting state.

Let us calculate and estimate the thermoelectric angle θ,[1] which characterizes the observed value of the magnetic flux produced under the influence of the temperature gradient. At $T\ll T_c$, if the relative change of temperature along the superconductor is small, the value of θ is estimated from formula (3.8) of[1]. At temperatures close to the transition point, the coefficient η is in this case not a smooth function and it cannot be taken outside the integral with respect to T. Using (22) and the expression for the number of superconducting electrons near T_c, we obtain

$$\theta \approx \frac{m}{e\hbar}\frac{T_c}{N_0}\eta_{s2}^{n}\left\{\ln\frac{T_c-T_1}{T_c-T_2}+2.2\frac{(1+d)}{(1+c)f}\left[\frac{2}{3}\left(\left(\frac{T_c-T_1}{T_c}\right)^2-\left(\frac{T_c-T_2}{T_c}\right)^2\right)\right.\right.$$
$$\times\ln\sigma^{-2}+\frac{2}{9}\left(\left(\frac{T_c-T_2}{T_c}\right)^2\ln\frac{T_c-T_2}{T_c}-\left(\frac{T_c-T_1}{T_c}\right)^2\ln\frac{T_c-T_1}{T_c}\right.$$
$$\left.\left.\left.-\frac{2}{3}\left(\frac{T_c-T_2}{T_c}\right)^3+\frac{2}{3}\left(\frac{T_c-T_1}{T_c}\right)^3\right)\right]\right\}. \qquad (25)$$

Substituting in the last expression $T_2\sim 0.95T_c$, $T_1\sim 0.93T_c$, $N_0\sim 10^{23}$ cm^{-3}, $\eta_{s2}^{n}=\alpha/\rho$, $\alpha=0.32$ μV/deg^2, $\rho/100n_{imp}=0.9$ $\mu\Omega$-cm/at.%, $\varepsilon_d\sim 0.1$ eV, $\Gamma\sim 10^{-2}$ eV, and $T_c\sim 1.3$ °K (this corresponds to the data for ThCe[9]), $N(0)\sim 0.1$ eV^{-1}, and $d\sim 5$, we find that at concentrations $n_{imp}\sim 10^{-5}=10^{-3}$ at.% we have $\theta\sim 10^{-2}$, which is experimentally feasible.[2] Allowance for the second term in the curly bracket leads to an increase of θ by an approximate factor of 3. With decreasing impurity concentration, θ increases in this case not only because of the decrease of ρ, but also because of the decrease of σ.

Measurements of the thermoelectric effect in superconductors containing a nonmagnetic impurity with a localized level can yield additional data on the nature of these impurities.

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[1] Yu. M. Gal'perin, V. L. Gurevich, and V. I. Kozub, Pis'ma Zh. Eksp. Teor. Fiz. **17**, 687 (1973) [JETP Lett. **17**, 476 (1973)]; Zh. Eksp. Teor. Fiz. **66**, 1387 (1974) [Sov. Phys.-JETP **39**, 680 (1974)].

[2] N. V. Zavaritskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **19**, 205 (1974) [JETP Lett. **19**, 126 (1974)].

[3] G. F. Zharkov and A. A. Sobyanin, *ibid.* **20**, 163 (1974) [**20**, 69 (1974]; V. L. Ginzburg, G. F. Zharkov, and A. A. Sobyanin, *ibid.* 20, 223 (1974) [**20**, 102 (1974)].

[4] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[5] L. M. Kovner, Zh. Eksp. Teor. Fiz. **65**, 307 (1973) [Sov. Phys.-JETP **38**, 151 (1974)].

[6] M. J. Zuckermann, Phys. Rev. **140A**, 899 (1965).

[7] A. B. Kaiser, J. Phys. C. **3**, 410 (1970).

[8] L. Z. Kon and V. A. Moskalenko Fiz. Tverd. Tela **16**, 2900 (1974) [Sov. Phys.-Solid State **16**, 1877 (1975)]; Fiz. Met. Metallov. **39**, 928 (1975); L. Z. Kon, Fiz. Tverd. Tela **16**, 1006 (1974) [Sov. Phys.-Solid State **16**, 650 (1974)].

[9] J. R. Cooper and C. Rizzuto, J. of low temp. Phys. **10**, 207 (1973).

[10] V. L. Ginzburg, Zh. Eksp. Teor. Fiz. **14**, 177 (1944).

[11] L. Z. Kon, Fiz. Tverd. Tela **17**, 1711 (1975) [Sov. Phys.-Solid State **17**, 1113 (1975)].

[12] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaleshinskiĭ, Metody kvantovoĭ teorii polya v statisticheskoĭ fizike, Fizmatgiz, 1962 (Quantum Field Theoretical Methods in Statistical Physics, Pergamon, 1965].

[13] V. A. Moskalenko, Metod issledovaniya plotnosteĭ élektronnykh sostoyaniĭ sverkhprovodyashichikh splavov (Method of Investigating the Densities of the Electronic States of Superconducting Alloys), Shtinitsa, 1974. N. I. Botoshan, V. A. Moskalenko, and A. M. Ursu, Teor. Mat. Fiz. **12**, 264 (1972).

[14] M. I. Vladimir, V. A. Moskalenko, and Yu. N. Nika, Teor. Mat. Fiz. **24**, 115 (1975). V. A. Moskalenko and M. I. Vladimir, Phys. Lett. **50A**, 353 (1974).

[15] H. Takayama and P. Fulde, Zeitschr. Physik **B20**, 81 (1975).

[16] A. G. Aronov, Zh. Eksp. Teor. Fiz. **67**, 178 (1974) [Sov. Phys.-JETP **40**, 90 (1975)].

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Current dependence of the microwave admittance of thin superconducting films

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The dependence of the microwave ($\omega/2\pi=9300$ MHz) admittance of thin (300–600 Å) superconducting Sn films on the temperature and on the direct current I is investigated. The films are 1–2 μ wide and 30–100 μ long. The measurements are performed at temperatures $T\approx(1.0–0.9)T_c$ and currents I of the order of the pair-breaking current I_c^{GL}. The experimental $\sigma_1(T)$ plot is in good quantitative agreement with the Mattis-Bardin theory; the slope of the plot is slightly less than the theoretical one. The $\sigma_2(I)$ plot at $I\lesssim I_c^{\mathrm{GL}}$ agrees with that predicted by the Ginzburg-Landau theory for $\omega\tau_\Delta\gg 1(\tau_\Delta)$ is the time of relaxation of the superconducting condensate to the equilibrium state). An estimate of the lower bound of τ_Δ is obtained ($\tau_\Delta\gg 10^{-11}$ sec at $T\gtrsim 0.9$ T_c).

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INTRODUCTION

The behavior of superconducting films in a weak high-frequency field is customarily described by the admittance $\sigma_s=\sigma_1-i\sigma_2$, which depends on the frequency ω. In the next higher approximation (in the absence of transport current) the admittance of the films is described by the Mattis–Barden theory.[1] If, however, the direct