SUPERCONDUCTORS CONTAINING IMPURITIES WITH AN INTERNAL DEGREE OF FREEDOM

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It is shown that introduction of an impurity with an internal degree of freedom into a superconductor alters significantly the spectrum of the superconductor, and gives rise in particular to gapless superconductivity. The appearance of a nonzero density of state inside the gap is the consequence of inelastic scattering of the electron by the impurities.

IT is well known that when nonmagnetic impurities are introduced into a superconductor, the spectrum of the superconductor and its thermodynamic properties remain practically unchanged. On the other hand, the presence of magnetic impurities greatly alters the spectrum of the superconductor[1]. In particular, at a certain concentration of such impurities, gapless superconductivity arises.

We show in this paper that when impurities with some internal degree of freedom are introduced into a superconductor, the electron spectrum can likewise be significantly altered. Let us consider first the physics of the occurrence of gapless superconductivity in the presence of such impurities. Let an electron be scattered by an impurity with an internal degree of freedom. Then, besides elastic scattering, scattering with excitation of the impurity is possible, and also scattering with transfer of the impurity from the excited state to the ground state. These processes, as can be shown, cause damping to appear in the Cooper pair, and this in turn leads to a vanishing of the gap in the spectrum. It is clear from the foregoing that the effect indicated above is a threshold one and that at zero temperature it does not exist, since there are no electrons capable of exciting the impurity at zero temperature, and all the impurities are in the ground state and cannot emit excitations. The law governing the temperature dependence of the density of states on the Fermi surface (and this is precisely the quantity that can be used conveniently to describe the magnitude of the effect) is essentially different, depending on whether the excitation transferred to the electron by the impurity has or has no damping. If there is no damping then, obviously, the density of states in the gap is exponentially small, since there exists an excitation threshold, but if the damping is present, then it can be readily seen that there is no threshold and the density of states in the gap depends on the temperature in power-law fashion.

We proceed now to a mathematical analysis of the problem. We use the following model: we assume that an impurity atom is present and that motion of this atom gives rise to a certain local oscillation. To describe this local oscillation, generally speaking, it is necessary to solve the equations of motion for the entire crystal with allowance for the impurity. We shall not do so, however, and assume that the phonon spectrum remains unchanged, while the impurity simply oscillates in the field of the neighboring atoms. This approximation, of course, is quite crude, but it is justified by the fact that the main effect is practically independent of the concrete form of the spectrum.

We assume a point interaction between the electrons and the impurity atoms. We choose the Hamiltonian of the interaction in the form

$$V=\int \psi^+(\mathbf{r})\psi(\mathbf{r})U(\mathbf{r})\,d\mathbf{r},$$

$$U(\mathbf{r})=\sum_i U(\mathbf{r}-\mathbf{r}_i),$$

$$U(\mathbf{r}_i)=-\frac{2\pi}{m}\left[a+\frac{b}{\sqrt{2}}(c_i+c_i^+)\right]\delta(\mathbf{r}-\mathbf{r}_i). \tag{1}$$

Here a is the electron-impurity elastic-scattering length, b the scattering length with production or absorption of the impurity excitation. c_i and c_i^+ the operators of annihilation and creation of the excitation of the i-th impurity, $\mathbf{r}_i$ the equilibrium position of the i-th impurity, m the electron mass, and $\psi(\mathbf{r})$ and $\psi^+(\mathbf{r})$ the second-quantized wave functions of the electron. We now need to calculate the electron Green's function and to average it over the impurities. We shall use an averaging technique analogous to that employed in the case of immobile scatterers[2,3]. To take into account the eigenlevels of the impurities, we used the method of introducing fictitious Fermi (or Bose) operators, employed, for example, in[4,5].

We introduce the Matsubara scattering matrix

$$\sigma(\tau)=T_\tau\exp\left\{-\int_0^\tau V(\tau')\,d\tau'\right\},$$

$$V(\tau)=e^{H_0\tau}Ve^{-H_0\tau}. \tag{2}$$

To calculate the Green's function we need the scattering matrix $\sigma(1/T)$[6]; its expansion in the perturbation-theory series yields

$$\sigma\left(\frac{1}{T}\right)=\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}\int_0^{1/T}d\tau_1\ldots\int_0^{1/T}d\tau_n\int d\mathbf{r}_1\ldots\int d\mathbf{r}_n$$
$$\times\sum_{i_1\ldots i_n}\langle T_\tau(\psi^+(\mathbf{r}_1,\tau_1)\psi(\mathbf{r}_1,\tau_1)U(\mathbf{r}_1-\mathbf{r}_{i_1},\tau_1)\ldots$$
$$\ldots\psi^+(\mathbf{r}_n,\tau_n)\psi(\mathbf{r}_n,\tau_n)U(\mathbf{r}_n-\mathbf{r}_{i_n},\tau_n))\rangle. \tag{3}$$

We substitute the obtained expression for the scattering matrix into the expression for the electron Green's function[6]

$$G(\mathbf{r}_1,\tau_1,\mathbf{r}_2,\tau_2)=-\frac{\langle T_\tau(\psi(\mathbf{r}_1,\tau_1)\psi^+(\mathbf{r}_2,\tau_2)\sigma(1/T))\rangle}{\sigma(1/T)}. \tag{4}$$

It is further necessary to carry out the usual transformations and to average over the positions of the impurities. We assume that the number of impurities is small and that p_0a, $p_0b \ll 1$, where p_0 is the Fermi momentum. We can then confine ourselves to the first order in the impurity concentration and to the second order in the interaction constant. As a result of simple calculations we obtain the following expression for the electron self-energy part:

$$M(p, i\omega) = -\frac{2\pi n}{m}a + \left(\frac{2\pi a}{m}\right)^2 n\int \frac{dq}{(2\pi)^3} G(q, i\omega)$$
$$-\left(\frac{2\pi b}{m}\right)^2 n \frac{T}{\omega_0}\sum_{\varepsilon}\int \frac{dq}{(2\pi)^3} G(q, i\varepsilon) L(i(\omega - \varepsilon)). \quad (5)$$

Here n is the impurity concentration, $i\omega$ and $i\epsilon$ are the Matsubara discrete frequencies, ω_0 the oscillation frequency of the impurity atoms, G(q, $i\omega$) the Fourier transform of the function G(r, τ), and L($i\omega$) the Fourier transform of the function L(τ), given by

$$L(\tau) = -{}^1/_2\omega_0\langle T_\tau\{c(\tau) + c^+(\tau)\}(c + c^+)\rangle. \quad (6)$$

The remaining analysis is determined completely by the form of the function L($i\omega$). If the impurity oscillates like a harmonic oscillator, without interacting with the surrounding atoms, then L($i\omega$) takes the form

$$L_0(i\omega) = \omega_0^2/[(i\omega)^2 - \omega_0^2]. \quad (7)$$

We now discuss the question of damping of the local oscillations. We have already mentioned that the damping of the local oscillations is extremely important for the temperature dependence of the density of states in the gap. We introduce the damping, for simplicity, by using a model, namely, we assume that L_0 is replaced by L defined by the formula

$$L^{-1} = L_0^{-1} - P. \quad (8)$$

We define P as follows:

$$P(i\omega) = -2i\alpha(i\omega)\omega_0^{-1}, \quad (9)$$

where $0 < \alpha < 1$. We then obtain

$$L = \frac{\omega_0^2}{(i\omega)^2 - \omega_0^2 - 2i\alpha(i\omega)\omega_0}. \quad (10)$$

We shall henceforth assume that α is small compared with unity.

We now proceed to solve the problem of scattering of an electron in a superconductor by such an impurity. It is easy to show (in analogy with the procedure used in superfluidity theory[7]) that the superconducting Green's functions (their definition is given, for example, in[6]) are equal to

$$G(i\omega) = \frac{i\tilde{\omega} + \tilde{\xi}}{(i\tilde{\omega})^2 - \tilde{\xi}^2 - \tilde{\Delta}(i\omega)\tilde{\Delta}(-i\omega)},$$
$$F(i\omega) = \frac{-\tilde{\Delta}(i\omega)}{(i\tilde{\omega})^2 - \tilde{\xi}^2 - \tilde{\Delta}(i\omega)\tilde{\Delta}(-i\omega)},$$

where

$$i\tilde{\omega} = i\omega - A(i\omega), \quad \tilde{\xi} = \xi - S(i\omega), \quad \tilde{\Delta} = \Delta + M_1(i\omega), \quad (12)$$
$$A(i\omega) = {}^1/_2[M(i\omega) - M(-i\omega)],$$
$$S(i\omega) = {}^1/_2[M(i\omega) + M(-i\omega)].$$

Here M($i\omega$) is defined in (5), and $M_1(i\omega)$ is equal to

$$M_1(i\omega) = \left(\frac{2\pi a}{m}\right)^2 n\int \frac{dq}{(2\pi)^3} F(q, i\omega)$$
$$-\left(\frac{2\pi b}{m}\right)^2 n\frac{T}{\omega_0}\sum_{\varepsilon}\int \frac{dq}{(2\pi)^3} F(q, i\varepsilon) L(i(\omega - \varepsilon)). \quad (13)$$

We note that the Green's functions G and F which enter in (5) and (13) are complete and not zero-valued. We put further

$$G(i\omega, p) = -\int d\omega' \frac{\rho(\omega', p)}{i\omega - \omega'}, \qquad L(i\omega) = -\int d\omega' \frac{\varphi(\omega', p)}{i\omega - \omega'}. \quad (14)$$

From (10) we get, taking (14) into account,

$$\varphi(\omega) = -\frac{\omega_0^2}{2\pi\varepsilon_0}\left\{\frac{\gamma_0}{(\omega - \varepsilon_0)^2 + \gamma_0^2} - \frac{\gamma_0}{(\omega + \varepsilon_0)^2 + \gamma_0^2}\right\},$$
$$\varepsilon_0 = \omega_0\sqrt{1 + \alpha^2}, \quad \gamma_0 = \alpha\omega_0. \quad (15)$$

If $|\alpha| \ll 1$, then $\epsilon_0 \approx \omega_0$.

From (5) we easily obtain, by analytic continuation with respect to ω, the following expression for $M^R(\omega)$ (the symbol R is used to denote retarded functions):

$$M^R(\omega) = -\frac{2\pi n}{m}a + \frac{2\pi n}{m}ia^2\tilde{g}(\omega)$$
$$+\frac{2nb^2}{m\omega_0}\int d\varepsilon_1 \int d\varepsilon_2 \operatorname{Re}\tilde{g}(\varepsilon_1)\varphi(\varepsilon_2)\frac{n(\varepsilon_1) - N(\varepsilon_2) - 1}{\omega - \varepsilon_1 - \varepsilon_2}; \quad (16)$$

here

$$\frac{m}{2\pi}i\tilde{g}(\omega) = \int \frac{dp}{(2\pi)^3}\int d\varepsilon \frac{\rho(\varepsilon, p)}{\omega - \varepsilon} = -\int \frac{dp}{(2\pi)^3} G^R(\omega, p), \quad (17)$$

with

$$n(\omega) = (e^{\omega/T} + 1)^{-1}, \quad N(\omega) = (e^{\omega/T} - 1)^{-1}. \quad (18)$$

We obtain analogously

$$M_1^R(\omega) = \frac{2\pi n}{m}ia^2\tilde{f}(\omega) - \frac{2nb^2}{m\omega_0}\int d\varepsilon_1 \int d\varepsilon_2.$$
$$\times \operatorname{Re}\tilde{f}(\varepsilon_1)\varphi(\varepsilon_2)\frac{n(\varepsilon_1) - N(\varepsilon_2) - 1}{\omega - \varepsilon_1 - \varepsilon_2}, \quad (19)$$
$$\frac{m}{2\pi}i\tilde{f}(\omega) = \int \frac{dp}{(2\pi)^3}(F^+)^R. \quad (20)$$

Taking into account the foregoing formulas, we can easily show that $M_1(-i\omega) = M_1(i\omega)$, while $A^R(\omega)$ and $S^R(\omega)$ are equal to

$$S^R(\omega) = -\frac{2\pi n}{m}a, \quad A^R(\omega) = M^R(\omega) - S^R(\omega). \quad (21)$$

It can also be shown that

$$\tilde{g}(\omega) = p_0\frac{\tilde{\omega}}{\sqrt{\tilde{\omega}^2 - \tilde{\Delta}^2}}, \quad \tilde{f}(\omega) = p_0\frac{\tilde{\Delta}}{\sqrt{\tilde{\omega}^2 - \tilde{\Delta}^2}}. \quad (22)$$

We now can readily obtain the following equations for $\tilde{\omega}$ and $\tilde{\Delta}$. Recognizing that $\varphi(-\epsilon) = -\varphi(\epsilon)$, we get

$$\tilde{\omega} = \omega + \frac{i\gamma}{p_0}\tilde{g}(\omega) + \frac{\Gamma_0}{\pi p_0\omega_0}\int d\varepsilon_1 \int d\varepsilon_2 \operatorname{Re}\tilde{g}(\varepsilon_1).$$
$$\times \varphi(\varepsilon_2)[n(\varepsilon_1) + N(\varepsilon_2)][\omega - \varepsilon_1 + \varepsilon_2]^{-1}, \quad (23)$$
$$\tilde{\Delta} = \Delta + \frac{i\gamma}{p_0}\tilde{f}(\omega) + \frac{\Gamma_0}{\pi p_0\omega_0}\int d\varepsilon_1 \int d\varepsilon_2 \operatorname{Re}\tilde{f}(\varepsilon_1).$$
$$\times \varphi(\varepsilon_2)[n(\varepsilon_1) + N(\varepsilon_2)][\omega - \varepsilon_1 + \varepsilon_2]^{-1};$$
$$\gamma = \frac{2\pi n}{m}p_0a^2, \quad \Gamma_0 = \frac{2\pi n}{m}p_0b^2. \quad (24)$$

Formulas (23) together with (22) constitute the equations for $\tilde{\omega}$ and $\tilde{\Delta}$.

Let us consider these equations first for the case when the local oscillation has no damping, i.e., at $\alpha = 0$. We then obtain from (23) and (15)

$$\tilde{\omega} = \omega + \frac{i\gamma}{p_0}\tilde{g}(\omega) - \frac{\Gamma_0}{2\pi p_0}\int d\varepsilon \operatorname{Re}\tilde{g}(\varepsilon)\left\{\frac{n(\varepsilon) + N(\omega_0)}{\omega - \varepsilon + \omega_0}\right.$$
$$\left. - \frac{n(\varepsilon) - N(\omega_0) - 1}{\omega - \varepsilon - \omega_0}\right\},$$

$$\tilde{\Delta} = \Delta + \frac{i\gamma}{p_0}\tilde{f}(\omega) - \frac{\Gamma_0}{2\pi p_0}\int d\varepsilon\, \mathrm{Re}\,\tilde{f}(\varepsilon)\left\{\frac{n(\varepsilon)+N(\omega_0)}{\omega-\varepsilon+\omega_0} - \frac{n(\varepsilon)-N(\omega_0)-1}{\omega-\varepsilon-\omega_0}\right\}. \quad (25)$$

To continue, it is necessary to make certain assumptions concerning the ratio of Δ and ω_0. Let us assume that $\Delta \ll \omega_0$. Further, we confine ourselves for simplicity to the calculation of the density of states at $\Delta = 0$, since the presence of a nonzero density of states at $\omega = 0$ indicates that there is no gap in the spectrum. We note that, as can be readily seen from (23), $\mathrm{Re}\,\tilde{g}(\epsilon)$ and $\mathrm{Im}\,\tilde{f}(\epsilon)$ are even functions of the real variable ϵ, while $\mathrm{Re}\,\tilde{f}(\epsilon)$ and $\mathrm{Im}\,\tilde{g}(\epsilon)$ are odd. Taking this circumstance into account, as well as the fact that because of the parity properties $\mathrm{Re}\,\tilde{\omega}(0) = \mathrm{Im}\,\tilde{\Delta}(0) = 0$, we obtain after simple calculations (we recall that the density of states is proportional to $\mathrm{Re}\,\tilde{g}(0)$)

$$\tilde{g}(0) = p_0\Gamma\{\Gamma^2 + (\Delta+\Omega)^2\}^{-1/2},$$

$$\tilde{f}(0) = -ip_0(\Delta+\Omega)\{\Gamma^2+(\Delta+\Omega)^2\}^{-1/2}; \quad (26)$$

$$\Gamma = \Gamma_0/\mathrm{sh}\frac{\omega_0}{T},\quad \Omega = -\frac{\Gamma_0}{\pi p_0}\int d\varepsilon\,\mathrm{Re}\,\tilde{f}(\varepsilon)\frac{n(\varepsilon)+N(\omega_0)}{\omega_0-\varepsilon}. \quad (27)$$

In the derivation of (26) we took into account the fact that $\mathrm{Re}\,\tilde{g}(\omega_0) \approx p_0$, since $\omega_0 \gg \Delta, \tilde{\Delta}$.

Let us discuss the results. We note first that there is a certain increment to Δ, due essentially to the fact that there is an additional branch of the vibrational spectrum, leading to additional attraction between the electrons. In addition, we see that the density of states at $\omega = 0$, which is proportional to $\mathrm{Re}\,\tilde{g}(0)$, differs from zero, i.e., gapless conductivity sets in. It is possible to calculate the density of states not only at $\omega = 0$, but also at other energies, but we shall not do so here, since the resultant formulas are quite cumbersome. We note only that, as already mentioned at the beginning of the article, for the case of an undamped local oscillation the quantity Γ, which is the main characteristic of the density of states in the gap, is exponentially small. For example, if $\Gamma \ll \Delta$ and $\omega_0 \gg T$, then

$$\tilde{g}(0) = \frac{2\Gamma_0}{\Delta+\Omega}p_0\exp\left(-\frac{\omega_0}{T}\right). \quad (28)$$

We now proceed to consider the case when the local oscillation has damping. We consider again only the value of the density of states at $\omega = 0$. It is easy to show that, owing to the parity, $\mathrm{Re}\,\tilde{\omega}(0) = \mathrm{Im}\,\tilde{\Delta}(0) = 0$. Further, it is seen that $\mathrm{Im}\,\tilde{g}(0) = \mathrm{Re}\,\tilde{f}(0) = 0$. Then we obtain from (23) Eq. (26), in which, however, Γ and Ω are determined not by (27), but by the expressions

$$\Gamma = -\frac{\Gamma_0}{p_0\omega_0}\int d\varepsilon\,\mathrm{Re}\,\tilde{g}(\varepsilon)\varphi(\varepsilon)\left(\mathrm{sh}\frac{\varepsilon}{T}\right)^{-1},$$

$$\Omega = \frac{\Gamma_0}{p_0\omega_0}\int d\varepsilon_1\int d\varepsilon_2\,\mathrm{Re}\,\tilde{f}(\varepsilon_1)\varphi(\varepsilon_2)\frac{n(\varepsilon_1)+N(\varepsilon_2)}{\omega-\varepsilon_1+\varepsilon_2}. \quad (29)$$

We are interested mainly in Γ and not in Ω; we shall therefore consider just this quantity. We note first that although $\varphi(\epsilon)$ is a resonant function with a maximum near $\epsilon = \omega_0$, at this maximum the term $[\sinh(\epsilon/T)]^{-1}$ is exponentially small (since $\omega_0 \gg T$), and therefore in fact the values of $\varphi(\epsilon)$ at $\epsilon \ll \omega_0$ are always significant; in this region we have

$$\varphi(\omega) = -2\alpha\omega/\pi\omega_0,\quad |\omega| \ll \omega_0. \quad (30)$$

We then get from (29)

$$\Gamma = \frac{2\alpha\Gamma_0}{\pi p_0\omega_0^2}\int \varepsilon\, d\varepsilon\,\mathrm{Re}\tilde{g}(\varepsilon)\left(\mathrm{sh}\frac{\varepsilon}{T}\right)^{-1}. \quad (31)$$

The calculation of Γ from (31) calls for first solving the equation for $\tilde{g}(\epsilon)$. For estimates, however, we can substitute for $\tilde{g}(\epsilon)$ the value of this function in the absence of impurities, and then we get

$$\Gamma = \frac{4\alpha\Gamma_0 T^2}{\pi\omega_0^2}\int_{\Delta/T}^{\infty}\frac{dx}{\mathrm{sh}\,x}\frac{x^2}{\sqrt{x^2-(\Delta/T)^2}}. \quad (32)$$

It is seen from (32) that when $\Delta \sim T$ we get $\Gamma \sim (T/\omega_0)^2$, and this leads to a power-law dependence on the temperature, rather than to the exponential dependence obtained when the local oscillations are undamped. We cannot state, however, that Γ depends on the temperature just quadratically, since no account was taken at all of the temperature dependence of the parameter α, which also depends on the temperature, as a rule in a power-law fashion, and the exponent depends already on the concrete conditions.

We shall now discuss the conditions under which the occurrence of gapless conductivity, which was discussed above, can be observed. Throughout the article we considered the case $\omega_0 \gg \Delta$, T. This condition, however, was assumed only to simplify the theoretical analysis of the problem and it not obligatory. On the other hand, if ω_0 is much larger than Δ and T, then it is seen from formulas (26) and (32) that Γ is very small. However, if ω_0 is small compared with Δ and T, then it is clear that the inelasticity effect simply drops out, so that it is desirable to have $\omega_0 \gtrsim \Delta T$.

We note that a contribution to Γ should be made also by acoustic phonons. However, their contribution is small because of the smallness of the corresponding phase volume.

The fact that inelastic scattering by impurities plays a principal role in the damping of the Cooper pairs is perfectly analogous to the fact that the inelastic scattering by the impurities makes an appreciable contribution to the low-temperature part of the resistance[8]. A more detailed analysis shows that both these phenomena are described by analogous formulas. We note only that γ, which is proportional to the residual resistance, does not enter the formulas for the density of states. The indicated analogy makes it possible to foresee that the effect predicted in the present article will become manifest most strongly in those cases when the temperature-dependent part of the impurity scattering, due to the inelastic scattering by the impurities, is sufficiently large at $T \sim \Delta$.

Taking into account the fact that $\Gamma \sim v_F/l_{in}$ (v_F—velocity on the Fermi surface, l_{in}—free path relative to inelastic processes), it is easy to estimate the order of magnitude of Γ from experiments on the measurement of the resistance, and also to choose alloys in which Γ is sufficiently large. From an analysis of the experimental data on low-temperature resistance it follows that Γ can be of the order of 1° and consequently, the density of states when $\omega < \Delta$ is sufficiently large.

We now consider the question of the experiment in which it is most convenient to observe the described effect. It can be observed, first of all, in ordinary tunnel

experiments. It is most convenient, in all probability, to observe it in experiments on the Josephson effect. The point is that in ordinary tunnel experiments, the tunnel current of the normal electrons interferes at finite temperatures. As to the Josephson effect, the phenomenon in question can lead, first, to a change in the temperature dependence of the current in the stationary Josephson effect, and second, to a broadening of the lines of the radiated electromagnetic radiation in the nonstationary Josephson effect. The point is that gapless conductivity, as can be readily shown, arises essentially as a result of the fact that the Cooper pair becomes, as it were, damped and the damping of the Cooper pair, in turn, should lead to a broadening of the Josephson line.

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