Nuclear spin relaxation in fine superconducting particles

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The density of states of electron excitations in fine superconducting particles is investigated on the basis of the thermodynamic fluctuation theory. In a narrow energy range near $\epsilon = \Delta_0$ the density is determined essentially by fluctuations of the order parameter. Nuclear spin relaxation is calculated over a broad temperature range by using the density of states thus found.

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1. The coherence of paired electrons in states with opposing spins in the superconducting phase makes the transitions of electrons interdependent in scattering in different initial and final states. Depending on the scattering mechanism, the processes divide into two types whose transition probabilities differ strongly because of the coherence effect. The first type is the ordinary potential interaction that leads to the absorption of longitudinal ultrasonic waves. The second type includes the hyperfine interaction of conduction electrons with nuclear spins, which determines the rate of the nuclear relaxation.

The rate of the nuclear relaxation for superconductors with a uniform gap diverges logarithmically, owing to the singularity in the density of electron states at the energy $\varepsilon = \Delta_0$ (Δ_0 is the gap in the electron spectrum). In real metals, however, the gap is anisotropic. Account of the anisotropy of the gap leads to a blurring of the singularity in the density of states near the threshold, so that the divergence is removed. Nevertheless, at temperatures close to T_c, the rate of the nuclear relaxation in superconducting states is greater than in the normal state near T_c. At low temperatures $\Delta_0(0) \gg T$, the rate of the nuclear relaxation falls off because of the absence of elementary excitations. Such a behavior of the nuclear relaxation rate was first observed by Hebel and Slichter.[1]

When the superconductors become dirty, the anisotropy of the gap is lessened. This leads to an increase in the nuclear relaxation rate in superconductors with increase in the amount of impurities introduced into them. The anisotropy effect is also suppressed in fine superconducting particles, when $d \ll \xi(T)$, (d is the linear dimension of the fine particles, $\xi(T)$ is the coherence length).

In the case of superconductors of very small dimensions, account of fluctuations of the order parameter is decisive in the determination of the nuclear relaxation rate, the more so that the anisotropy of the gap decreases with increase in the concentration of the ordinary impurities and with decrease in the dimensions of the sample. The present work is devoted to the study of the effect of fluctuation oscillations of the order parameters on the density of electron states and on the relaxation of the nuclear spin in fine superconducting particles. We shall study cases of dirty superconductors $l \ll d \ll \xi(T)$, where l is the free path length of the electrons.

2. To investigate the role of fluctuations of the order parameter in the change of the density of electron states, we proceed in the following manner. We introduce the fluctuation increment of the order parameter

$$\Delta(t)=\Delta_0+\Delta_1(t), \tag{1}$$

where Δ_0 is the equilibrium value of the gap and $\Delta_1(t) \ll \Delta_0$. Using the time-dependent Gor'kov equation, integrated over the energy variable[2,3] $\xi = v_0(p-p_0)$ (v_0 and p_0 are the Fermi velocity and momentum), with account of electron-phonon interaction, it is not difficult to obtain a linear equation for the fluctuation correction in the case of fine dirty superconducting particles:

$$(-i\omega+\lambda)\Delta_1(\omega)=y_\omega,$$
$$\lambda=\begin{cases}7\zeta(3)\Delta_0(T)/\pi^3T_c\tau_0, & \Delta_0(T)\ll T_c\\ 4\pi T/(\pi^2-4)\Delta_0(0)\tau_0, & \Delta_0(0)\gg T\end{cases}; \tag{2}$$

here τ_0 is the relaxation time, associated with inelastic electron-phonon interaction, equal in order of magnitude to Θ^2/T^3 (Θ is the Debye energy).

In (2), we have added the random force y_ω in analogy with the method used by Langevin in the theory of Brownian motion. The method of random Langevin forces was used by Aronov and Katilyus[4] for the investigation of fluctuation oscillations in pure superconductors. To find the correlator of the random forces, we use the scheme of Onsager.[5] We investigate the change in the free energy of the system due to the fluctuations. The free energy as a functional of the order parameter and the Green's functions (integrated over the energy variable) takes in the absence of an external electromagnetic field the form[6]

$$\Omega=\int dV\Big\{\frac{|\Delta|^2}{\lambda_{eff}}-2\pi\nu T\sum_{n>0}\int\frac{do_p}{4\pi}\Big[\Delta^*f_p+\Delta f_p^+ +2\varepsilon_n(g_p-1)+\frac{1}{2}g_p\mathbf{v}\frac{\partial}{\partial\mathbf{r}}\ln\frac{f_p}{f_p^+}+\frac{1}{2\tau}\int\frac{do_{p'}}{4\pi}\Big(\frac{1}{2}f_pf_{p'}^+ +\frac{1}{2}f_p^+f_{p'}+g_pg_{p'}-1\Big)\Big]\Big\}, \tag{3}$$

where $g_p=(1-f_pf_p^+)^{1/2}$, $\nu=mp_0/2\pi^2$ is the density of electron states on the Fermi surface, λ_{eff} = the BCS constant, $\varepsilon_n=\pi T(2n+1)$, and $\tau=l/v_0$ is the time between collisions. In formula (3) we assume for simplicity short-range scattering of the electrons by impurities.

We limit ourselves to dirty superconductors; therefore, if we set in (3)

$$g_{\mathbf{p}}=g+\frac{\mathbf{p}}{p_0}\mathbf{g},\quad f_{\mathbf{p}}=f+\frac{\mathbf{p}}{p_0}\mathbf{f},\quad f_{\mathbf{p}}^{+}=f^{+}+\frac{\mathbf{p}}{p_0}\mathbf{f}^{+},\tag{4}$$

use the equations obtained for the Green's functions from the condition that (3) be a minimum, and integrate over the angles, we obtain

$$\Omega=\int dV\left\{\frac{|\Delta|^2}{\lambda_{eff}}-2\pi\nu T\sum_{n>0}\left[\Delta^{*}f+\Delta f^{+}+2\varepsilon_n(g-1)+\frac{D}{4}ff^{+}\left(\frac{\partial}{\partial\mathbf{r}}\ln\frac{f}{f^{+}}\right)^2-\frac{D}{2}g\frac{\partial}{\partial\mathbf{r}}\left(\frac{1}{g}\frac{\partial}{\partial\mathbf{r}}\ln ff^{+}\right)\right]\right\},\tag{5}$$

where $D=v_0 l/3$ is the diffusion coefficient.

In the following, it is necessary to find the second variation of the free energy. For this purpose, we must linearize the equation for the Green's functions in the small additions to the equilibrium values of the Green's functions and the order parameter, express the small additions to the Green's functions in terms of the small additions to the order parameter and, substituting them in the second variation of the free energy, obtain a functional that is quadratic in the small addition to the order parameter. Omitting all the intermediate calculations, we write out the expression for the second variation of the free energy in the case of fine superconducting particles:

$$\delta^2\Omega=\nu d^3\left\{\ln\frac{T}{T_c}-2\pi T\sum_{n>0}\left[\frac{\varepsilon_n^2}{(\varepsilon_n^2+\Delta_0^2)^{3/2}}-\frac{1}{\varepsilon_n}\right]\right\}\Delta_1^2;\tag{6}$$

d^3 is the volume of the sample. In obtaining this relation, it is assumed that the order parameter is real. We have also used the relation

$$\frac{1}{\lambda_{eff}}=\nu\left(\ln\frac{T}{T_c}+2\pi T\sum_{n>0}\frac{1}{\varepsilon_n}\right)\tag{7}$$

with the standard cutoff of the summation in (7).

Introducing the generalized coordinate $x=\Delta_1$ and the generalized force corresponding to it

$$X=T^{-1}\partial\delta^2\Omega/\partial x,$$

we obtain

$$X=\beta\Delta_1=-\frac{2\nu d^3}{T}\left\{\ln\frac{T_c}{T}+2\pi T\sum_{n>0}\left[\frac{\varepsilon_n^2}{(\varepsilon_n^2+\Delta_0^2)^{3/2}}-\frac{1}{\varepsilon_n}\right]\right\}\Delta_1.\tag{8}$$

Using (2) and (8), we obtain

$$-i\omega\Delta_1(\omega)=-\gamma X(\omega)+y_\omega,\qquad \gamma=\lambda/\beta.\tag{9}$$

The correlator of the random force introduced by us in Eq. (2) is determined by the coefficient γ (see Ref. 5): $\langle y^2\rangle_\omega=2\gamma$. The Fourier transformation of the correlator of the fluctuation correction to the order parameter is determined in the following fashion:

$$\langle\Delta_1^2\rangle_\omega=\langle\Delta_1(\omega)\Delta_1(-\omega)\rangle=2\gamma/(\omega^2+\lambda^2).\tag{10}$$

The correlator of the fluctuation correction of the order parameter can be obtained by integration with respect to the frequency of the expression (10): $\langle\Delta_1^2\rangle=1/\beta$. The limiting values of the correlator $\langle\Delta_1^2\rangle$ have the following form, as is readily seen from Eq. (8):

$$\langle\Delta_1^2\rangle=\begin{cases}2\pi^2T_c^3/7\zeta(3)\nu d^3\Delta_0^2(T) & \Delta_0(T)\ll T_c\\ T/2\nu d^3 & \Delta_0(0)\gg T\end{cases}.\tag{11}$$

Naturally, the condition of smallness of the fluctuations $\langle\Delta_1^2\rangle^{1/2}\ll\Delta_0(T)$ must be satisfied in this case.[1)]

3. In our approach, in the calculation of the correlator $\langle\Delta_1^2\rangle$ it was always understood that the time for establishment of partial equilibrium (at a given value of Δ_1) is much smaller than the time of establishment of the equilibrium value of the quantity Δ_1 ($\overline{\Delta}_1=0$). The time of establishment of the equilibrium value of Δ_1, as is seen from Eq. (2), is determined by the interaction of the electrons with the phonon thermostat and is equal to λ^{-1}. This time is much larger than all the characteristic times of the superconductor. Therefore, to determine the mean density of states from the fluctuations, we must average the local (in time) density of states over all possible values of Δ_1. For the probabilities of the fluctuations of Δ_1, we use the Gaussian distribution[2)]

$$w(\Delta_1)=(2\pi\langle\Delta_1^2\rangle)^{-1/2}\exp\{-\Delta_1^2/2\langle\Delta_1^2\rangle\}.\tag{12}$$

We note that we obtain this result directly if we assume that the probability of realization of the state $\Delta_0+\Delta_1$ is proportional to $\exp\{-R_{min}(\Delta_1)/T\}$, where $R_{min}(\Delta_1)$ is the minimum work necessary for the transition of the system from the state with an order parameter Δ_0 to $\Delta_0+\Delta_1$. This is determined in our case by the formula (6), which leads directly to (12).

The averaging of the density of electron states over the Gaussian distribution in the case of inhomogeneous superconductors has been done by Larkin and Ovchinnikov.[7] The averaged density of electron states over the distribution (12) in all regions of the energy is

$$\begin{aligned}\langle\nu_s\rangle&=\frac{\nu}{2}\left(\frac{\varepsilon}{\Delta_0-\varepsilon}\right)^{1/2}\exp\left\{-\frac{(\varepsilon-\Delta_0)^2}{2\langle\Delta_1^2\rangle}\right\},\quad \Delta_0-\varepsilon\gg\langle\Delta_1^2\rangle^{1/2},\\ \langle\nu_s\rangle&=\frac{\nu}{2}\left(\frac{\Delta_0^2}{\langle\Delta_1^2\rangle}\right)^{1/4}D_{-1/2}\left(\frac{\Delta_0-\varepsilon}{\langle\Delta_1^2\rangle^{1/2}}\right)\exp\left\{-\frac{(\varepsilon-\Delta_0)^2}{4\langle\Delta_1^2\rangle}\right\},\quad |\varepsilon-\Delta_0|\ll\Delta_0,\\ \langle\nu_s\rangle&=\nu\varepsilon/(\varepsilon^2-\Delta_0^2)^{1/2},\quad \varepsilon-\Delta_0\gg\langle\Delta_1^2\rangle^{1/2}.\end{aligned}\tag{13}$$

Here $D_{-1/2}(x)$ is a parabolic-cylinder function. The averaged density of states is finite in the entire energy region. The maximum of the density of states shifts towards higher energy and its maximum is of the order of $\langle\nu_s\rangle/\nu\sim(\Delta_0/\langle\Delta_1^2\rangle^{1/2})^{1/2}$. The width of the interval of energy near threshold in which the density of states changes significantly in the averaging is of the order of $\langle\Delta_1^2\rangle^{1/2}$.

4. We calculate the rate of nuclear relaxation of fine superconducting particles. For this we use the formula of Ref. 1:

$$\frac{R_s}{R_n}=-2\int_0^\infty d\varepsilon\frac{df(\varepsilon)}{\partial\varepsilon}\left(1+\frac{\Delta_0^2}{\varepsilon^2}\right)\frac{\langle\nu_s\rangle^2}{\nu^2}.\tag{14}$$

In the experiment one measures the time T_{1s} of establishment of equilibrium of the nuclear spins with the electron spins at zero magnetic field. If we introduce the time T_{1n} of nuclear relaxation in the normal state, we can then write

$$T_{1n}/T_{1s}=R_s/R_n,$$

where R_s is the nuclear relaxation rate in the superconductor, R_n is the nuclear relaxation rate in the normal state at a temperature close to T_c, and $f(\varepsilon)$ is the Fermi distribution.

Omitting the calculation of the integral (14) with use of (13), we give the result for the nuclear relaxation rate in the region of high temperatures $\Delta_0(T)\ll T_c$:

$$\frac{R_s}{R_n}=2f(\Delta_0)+\frac{2\Delta_0}{T}f(\Delta_0)(1-f(\Delta_0))\ln\frac{\Delta_0}{\langle\Delta_1^2\rangle^{1/2}}. \qquad (15)$$

We note that this result is valid with accuracy to a numerical coefficient under the logarithm.

Using the averaged density of states (13), we also calculate the ultrasonic absorption in fine superconducting particles. We can obtain the formula for the ratio α_s/α_n (α_s and α_n are the coefficients of sound absorption in the superconducting and normal states) from Eq. (14) by replacing the factor $1+\Delta_0^2/\varepsilon^2$ under the integral by $1-\Delta_0^2/\varepsilon^2$. It is easy to see that, within the limits of accuracy of our estimates, the ratio α_s/α_n for fine superconducting particles will not differ from the well known expression

$$\alpha_s/\alpha_n=2f(\Delta_0)$$

for superconductors with constant gap Δ_0.

The logarithm in Eq. (6) contains a large parameter that depends strongly on the size of the samples. The condition $\Delta_0(T)\gg\langle\Delta_1^2\rangle^{1/2}$ can be rewritten in the following fashion, as is easily seen from (11), at temperatures close to the critical:

$$\varepsilon_0^{1/2}\equiv(\nu d^3)^{-1/2}\ll\Delta_0^2(T)/T_c^{3/2}$$

which in turn imposes an additional limitation on the size of the samples

$$(\xi_0/d)^{3/2}\ll\Delta_0^2(T)\varepsilon_F T_c^{-3}\ (\xi_0\sim v_0/T_c).$$

This condition is not satisfied for fine particles in the immediate vicinity of T_c because of the high intensity of the fluctuations. The expression (15) has a characteristic temperature dependence, which can be measured experimentally, of the nuclear relaxation rate.

It is seen from expressions (15) and (11) that the nuclear relaxation rate of fine superconducting particles does not depend on the impurity concentration. Butterworth and McLaughlin[8] carried out measurements of the quantity $[R_s(T)]_{max}/R_s(T_c)$ ($[R_s(T)]_{max}$ is the value of the nuclear relaxation rate at the maximum) as a function of the quantity $1/\Delta_0(0)\tau$ ($\tau=l/v_0$ is the time between collisions by ordinary impurities) on pure and dirty samples. Within the limits of experimental error, the ratio $[R_s(T)]_{max}/R_s(T_c)$ did not depend on the concentration of impurities. However, it must be noted that the condition of smallness of the samples was not rigorously observed. In the experiments mentioned, $d\sim\xi_0$.

Finally, we give the results for the nuclear relaxation rates at low temperatures $\Delta_0(0)\gg T$. A simple estimate shows that at the accuracy assumed by us we have at low temperatures,

$$\frac{R_s(T)}{R_n}=\frac{2\Delta_0(0)}{T}\ln\frac{T}{\langle\Delta_1^2\rangle^{1/2}}\exp\left\{-\frac{\Delta_0(0)}{T}\right\}. \qquad (16)$$

In obtaining this result, it is assumed that, in addition to $\Delta_0(0)\gg T$, the condition $T\gg\langle\Delta_1^2\rangle^{1/2}$ is also satisfied. Consideration of lower temperatures $T\ll\langle\Delta_1^2\rangle^{1/2}$ is not possible, since the latter condition (see (11)) means that $\varepsilon_0^{1/2}=(\nu d^3)^{-1/2}\gg T^{1/2}$, where ε_0 is of the order of the distance between the energy levels of the fine metallic particles. When the distance between the levels becomes greater than the temperature of the sample, it is necessary to take quantum size effects into account.

In conclusion, I wish to express my gratitude to A. G. Aronov for interesting discussions.

1) At the same time, the fluctuations of Δ must exceed its scatter due to its anisotropy, the dependence on the size of the granules, on the local temperature, and so on.

2) It is understood here that the phase space of the fluctuations of the gap is given by $d\Gamma=\text{const.}\,d\Delta_1$, i.e., it is assumed that allowance for the fluctuations of the phase of the order parameter is unimportant.

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