Fluctuation shift of the transition temperature of thin superconducting films

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An expression for the superconducting transition temperature of thin films due to fluctuations of the order parameter Δ and electromagnetic field is derived. The effect of size quantization on T_c is considered.

1. INTRODUCTION

The properties of thin superconducting films have been widely investigated in recent years both experimentally and theoretically. The superconducting transition temperature of thin films can be either higher or lower than T_c of the bulk sample[1,2]. One of the causes of the dependence of T_c on the film thickness is the presence of fluctuations of the order parameter Δ and of the electromagnetic field[2,3]. In addition to the fluctuations, there are also other factors leading to a dependence of T_c on the film thickness, such as the change of the phonon spectrum, the influence of the substrate, and quantization in the transverse direction[2,4,5]. These lead to a shift of T_c, which in many cases is larger than the fluctuation correction to the transition temperature.

We consider here the influence of the fluctuations and of the size quantization on the superconducting transition temperature of thin films.

2. EFFECT OF FLUCTUATIONS ON T_c

To calculate the fluctuation shift of the transition temperature we use a previously developed method[6]. It is meaningful to consider the fluctuation shift of the transition temperature only in the case of small free paths $l \ll d$ (d is the film thickness), since in all remaining cases it is certainly smaller than the shift of T_c due, for example, to size quantization. In the case of much "dirt," the Gor'kov equation can be reduced to the equations for the Green's functions in coinciding points[6]:

$$\tau_z \frac{\partial G}{\partial \tau} + \frac{\partial G}{\partial \tau'}\tau_z + [e\varphi - \hat{\Delta}, G] = -iD\left[\frac{\partial}{\partial \mathbf{R}} - ie\mathbf{A}\tau_z, G\left(\frac{\partial}{\partial \mathbf{R}} - ie\mathbf{A}\tau_z\right)G\right] + \frac{i}{2\tau_s}[\tau_z, G\tau_z G] + eD\tau_z\delta(\tau-\tau')\,\mathrm{div}\,\mathbf{A};$$

$$\int_0^{1/T} G(\tau, \tau_1, \mathbf{R})G(\tau_1, \tau', \mathbf{R})\,d\tau_1 = \delta(\tau - \tau'); \tag{1}$$

$$G = \begin{pmatrix} g_1; & F_1 \\ -F_2; & g_2 \end{pmatrix} \equiv \frac{i}{\pi\nu}G(\tau, \tau', \mathbf{R}, \mathbf{R}),$$

$$\hat{\Delta}(\mathbf{r}, \tau) = \begin{pmatrix} 0; & \Delta_1(\mathbf{r}, \tau) \\ -\Delta_2(\mathbf{r}, \tau); & 0 \end{pmatrix} \tag{2}$$

$$\Delta_{1,2}(\mathbf{r}, \tau) = i\pi\nu|\lambda|F_{1,2}(\tau, \tau, \mathbf{r}),$$

where τ_z is a Pauli matrix, τ_s is the path time of electrons with spin flip, $D = v l_{tr}/3$ is the diffusion coefficient, $\nu = mp/2\pi^2$ is the density of states on the Fermi surface, and [..., ...] is a commutator. The time arguments in (1) stand in the order in which the operators are written out, for example,

$$AG \equiv A(\tau)G(\tau, \tau'), \quad GG \equiv \int_0^{1/T} G(\tau, \tau_1)G(\tau_1, \tau')\,d\tau_1. \tag{3}$$

The current density $\mathbf{j}$ and the charge density ρ are expressed in terms of the Green's function G in accordance with the formula

$$\mathbf{j}(\tau) = \pi\sigma_0\left\{-\mathbf{A}(\tau)\delta(\tau - \tau') + \frac{i}{2e}\mathrm{Sp}\,\tau_z\int_0^{1/T} G(\tau, \tau_1)\left(\frac{\partial}{\partial \mathbf{r}} - ie\mathbf{A}(\tau_1)\tau_z\right)G(\tau_1, \tau')\,d\tau_1\right\}_{\tau'=\tau}, \tag{4}$$

$$\rho(\tau) = -e\nu\{2e\varphi(\tau) + i\pi\,\mathrm{Sp}\,G(\tau, \tau')\}_{\tau=\tau'},$$

where $\sigma_0 = p^2e^2l_{tr}/3\pi^2$ is the residual conductivity of the normal metal.

To find the fluctuation shift of the transition temperature it is necessary to find the function $F_1(\tau, \tau)$ with allowance for the fluctuations. Without account of the fluctuations we have

$$F_1(\omega) = -i\Delta/|\omega|. \tag{5}$$

From formulas (2) and (5) we obtain for the fluctuation shift of the transition temperature of a thin film ($d \ll \xi$)

$$-\frac{\delta T_c}{T_c} = \frac{T_c^0 - T_c}{T_c^0} = -i\pi T^2\sum_{\omega,\omega_0}\frac{1}{d}\int\frac{d^2\mathbf{k}}{(2\pi)^2}\frac{1}{\Delta}\langle F_1^{(2)}(\omega, \omega_0)\rangle, \tag{6}$$

where $F_1^{(2)}(\omega, \omega_0)$ is the second-order correction (in the fluctuations) to the function F_1.

It is convenient to perform all the remaining calculations in the gauge div $\mathbf{A} = 0$. The function $\langle F_1^{(2)}\rangle$ is obtained from the system (1) by simple perturbation-theory expansion up to second order in the fluctuation fields of Δ_1, Δ_2, φ, and $\mathbf{A}$. Performing this expansion, we obtain after simple calculations

$$\begin{aligned}
-\frac{i}{\Delta}\langle F^{(2)}_{1(\omega,\omega_0)}\rangle = {} & \frac{\langle\Delta_1(\omega_0)\Delta_2(-\omega_0)\rangle}{|\omega|}\left[\frac{1 + \mathrm{sign}\,\omega\,\mathrm{sign}\,\omega_+}{(D\mathbf{k}^2 + |\omega| + |\omega_+|)^2} + \frac{\mathrm{sign}\,\omega_+}{\omega(D\mathbf{k}^2 + |\omega| + |\omega_+|}\right] - \frac{2ie\,\mathrm{sign}\,\omega_+\langle\varphi_{\omega_0}\Delta_1(-\omega_0)\rangle}{\Delta|\omega|(D\mathbf{k}^2 + |\omega| + |\omega_+|)} \\
& + \frac{e^2\langle\varphi_{\omega_0}\varphi_{-\omega_0}\rangle}{|\omega|}\left[\frac{\omega_0}{\omega|\omega_+|(D\mathbf{k}^2 + |\omega| + |\omega_+|)} - \frac{1 - \mathrm{sign}\,\omega\,\mathrm{sign}\,\omega_+}{(D\mathbf{k}^2 + |\omega_0|)^2}\right] + \frac{e^2D(2\omega + \omega_0)}{\omega|\omega||\omega_+|}\langle A_{\omega_0}A_{-\omega_0}\rangle,
\end{aligned} \tag{7}$$

$$\omega_+ = \omega + \omega_0.$$

The correlation functions in (7) were calculated earlier[6]. In the principal approximation in Δ, their values are

$$\begin{aligned}
\langle\Delta_1(\omega_0)\Delta_2(-\omega_0)\rangle &= \nu^{-1}\left\{\psi\left(\frac{1}{2} + \frac{|\omega_0| + D\mathbf{k}^2}{4\pi T}\right) - \psi\left(\frac{1}{2}\right)\right\}^{-1}, \\
\langle\varphi_{\omega_0}\varphi_{-\omega_0}\rangle &= \left\{\frac{\mathbf{k}^2}{4\pi} + \frac{2e^2\nu D\mathbf{k}^2}{|\omega_0| + D\mathbf{k}^2}\right\}^{-1}, \\
\frac{1}{\Delta}\langle\varphi_{\omega_0}\Delta_1(-\omega_0)\rangle &= \frac{i\,\mathrm{sign}\,\omega_0}{e\nu D\mathbf{k}^2(|\omega_0| - D\mathbf{k}^2)} \\
&\times\left\{|\omega_0| - D\mathbf{k}^2\frac{\psi(1/2 + |\omega_0|/2\pi T) - \psi(1/2)}{\psi(1/2 + (|\omega_0| + D\mathbf{k}^2)/4\pi T) - \psi(1/2)}\right\},
\end{aligned} \tag{8}$$

$$\langle A_{\omega_0}{}^i A_{-\omega_0}^j\rangle = \left(\delta_{ij} - \frac{k_i k_j}{\mathbf{k}^2}\right)\left\{\frac{\mathbf{k}^2+\omega_0^2}{4\pi} + \sigma_0\left(|\omega_0| + \frac{\pi\Delta^2}{2T}\right)\right\}^{-1}.$$

With logarithmic accuracy we obtain from formulas (6)—(8) for thin films ($d \ll \xi$)

$$-\frac{\delta T_c}{T_c} = \frac{21\zeta(3)}{2\pi^2 p^2 l_{tr} d}\ln(p^2 l_{tr} d) - \frac{1}{4p^2 l_{tr} d}\left[\ln\left(\frac{v l_{tr}}{d^2 T}\right)\right]^3 + \frac{\pi e^2 v l_{tr}}{12d}\left\{\ln\left(\frac{1}{Te^2 d}\right) + \frac{2}{3\pi^2}\left[\ln\left(\frac{1}{e^2 d^2 p^2 l_{tr} T}\right)\right]^3\right\}. \quad (9)$$

The first term in (9) is connected with the fluctuations of the order parameter Δ, and the last term is connected with fluctuations of the vector potential **A**. The second term in this formula is the result of fluctuations of the scalar potential φ and of the crossing term $\langle\Delta\varphi\rangle$. The main contribution to the second term is made by high frequencies $\omega_0 \gg T$. The contribution of the zero frequency $\omega_0 = 0$ to the second term, as follows from (7) and (8), is zero. The first term of (9) was obtained in the paper by Strongin et al.[2]

For a film, the region τ_0 of smearing of the phase transition is given by

$$\tau_0 = 3\pi^2 / 16p^2 l_{tr} d \quad (10)$$

and is logarithmically small (in comparison with the fluctuation shift $\delta T_c/T_c$ determined by formula (9)).

The ratio of the coefficients of the logarithms of the first and third terms is equal to $2\kappa^2$, where $\kappa = \lambda/\xi$ is the parameter of the Ginzburg-Landau theory. For highly "dirty" superconductors we have $\kappa \gg 1$ and the third term can be neglected in comparison with the first. Using expression (10) for τ_0 and omitting the last term of (9), we obtain for the fluctuation shift δT_c

$$-\frac{\delta T_c}{T_c} = \frac{56\zeta(3)}{\pi^4}\tau_0 \ln\left(\frac{1}{\tau_0}\right) - \frac{4\tau_0}{3\pi^2}\left[\ln\left(\frac{v l_{tr}}{d^2 T}\right)\right]^3. \quad (11)$$

For granules and filaments, the fluctuation shift $\delta T_c/T_c$ of the transition temperature in the region of smearing of the phase transition turns out to be of the same order, namely for a filament

$$-\frac{\delta T_c}{T_c} \sim \tau_0 = \left(\frac{\pi^7}{2^{11}(mpS)^2 DT}\right)^{1/3}, \quad (12a)$$

where S is the filament cross section area, and for a granule

$$-\frac{\delta T_c}{T_c} \sim \tau_0 = \pi\left(\frac{2v}{TVp^2}\right)^{1/2}, \quad (12b)$$

where V is the volume of the granule.

3. EFFECT OF QUANTIZATION ON THE SHIFT T_c

The effect of the finite dimensions of a superconductor on the transition temperature was considered by a number of workers[2,4,5], but their results do not agree. Parmenter[5] considered the rise of T_c due to the discrete character of the spectra in a small-sized sample. It turned out to be very small and proportional to $(pR)^{-2}\xi_0/R$. The reason was that Parmenter used in[5] periodic boundary conditions. More realistic boundary conditions leads to a much larger shift T_c. In the other studies[2,4], the signs of the shift T_c were opposite. It is therefore meaningful to return once more to this question.

We consider the simplest model of a pure film with zero boundary conditions. It can be shown that both limitations, namely the addition of impurities and the replacement of a zero boundary condition by a more realistic one, i.e., a potential jump of finite height, are negligible and do not change the picture qualitatively. The equation for determining T_c is[7]

$$\Delta(z) = |\lambda| T \sum_\omega \sum_{n,n_1=1}^{\infty} \int \frac{d^2\mathbf{k}}{(2\pi)^2}\varphi_n(z)\varphi_{n_1}(z) \times \frac{\xi_n\xi_{n_1}+\omega^2}{(\xi_n^2+\omega^2)(\xi_{n_1}^2+\omega^2)}\int_0^d dz_1 \varphi_n(z_1)\Delta(z_1)\varphi_{n_1}(z_1), \quad (13)$$

where φ_n are normalized functions satisfying the equation

$$\left[-\frac{1}{2m}\frac{\partial^2}{\partial z^2} + V(z)\right]\varphi_n = E_n\varphi_n$$

with boundary conditions $\varphi(0) = \varphi(d) = 0$ and $\xi_n = \mu - \mathbf{k}^2/2m - E_n$. The potential $V(z)$ includes the electric field due to the separation of the charges and connected with the size quantization.

We seek the solution of (13) in the form

$$\Delta(z) = \langle\Delta\rangle + \Delta_1(z). \quad (14)$$

The correction $\Delta_1(z)$ is small only over distances on the order of p^{-1} from the boundary. By calculating $\Delta_1(z)$ by perturbation theory and averaging Eq. (13) over the coordinates, we obtain

$$1 = |\lambda| T \sum_\omega \frac{m}{4|\omega| d}\left[1 + \sum_{n=1}^{\infty}\left(1 + \frac{2}{\pi}\operatorname{arctg}\frac{\mu - E_n}{|\omega|}\right)\right]. \quad (15)$$

Substituting μ and E_n in (15) in the form

$$\mu = \mu_0 + \mu_1, \quad E_n = \frac{1}{2m}\left(\frac{\pi n}{d}\right)^2 + E_n^{(1)}, \quad (16)$$

where μ_0 is the value of the chemical potential as $d \to \infty$, we obtain

$$1 = |\lambda| T \sum_\omega \frac{m(2m\mu_0)^{1/2}}{2\pi|\omega|} + \frac{1}{2}\frac{\mu^{(1)} - E_{ph}^{(1)}}{\mu}, \quad (17)$$

where $E_{ph}^{(1)}$ is the correction to the energy at $n = pd/\pi$.

We have left out from (17) a term that oscillates with thickness at distances on the order of p^{-1}. When averaging over interatomic distances through the thickness, the contribution of this term to the right-hand side of (17) is smaller than or equal to $(pd)^{-2}$.

From (17) we obtain for the shift of T_c

$$\frac{\delta T_c}{T_c} = (\mu^{(1)} - E_\Phi^{(1)})\frac{\partial}{\partial\mu}\ln T_c. \quad (18)$$

The expression for the correction to the chemical potential $\mu^{(1)}$ can be obtained from the condition that the average electron density be conserved[7]

$$\langle n(z)\rangle = -2T\left\langle \sum_\omega \int \frac{d^2\mathbf{k}}{(2\pi)^2}\sum_{n=1}^{\infty}\varphi_n^2(z)\frac{\xi_n + i\omega}{\xi_n^2+\omega^2}e^{i\omega\delta}\right\rangle. \quad (19)$$

Summing over ω in (19) and omitting the oscillating increments, we obtain from (16) and (19)

$$\int_0^{\mu=E_y} (\mu^{(1)} - E_y^{(1)})\,dy = \mu/2. \quad (20)$$

If the Coulomb interaction is not taken into account or if $\kappa_D \sim p$, the integrand in (20) is independent of y at $y \sim pd$, and in this case we obtain for the size-effect transition-temperature shift the expression

$$\frac{\delta T_c}{T_c} = \frac{\pi}{2pd}\mu\frac{\partial \ln T_c}{\partial\mu}. \quad (21)$$

In real superconductors with $\kappa_D \sim p$, the jump of the potential on the boundary is finite. All this leads to the appearance of a numerical factor $\alpha \sim 1$ in the right-hand side of (21). When d^{-1} is replaced by the ratio S/V, where S is the particle area and V is its volume, formula (21) holds, in order of magnitude, for a particle of arbitrary shape.

In the BCS model we have

$$\mu\frac{\partial \ln T_c}{\partial\mu}=\frac{1}{2}\ln\frac{2\gamma\omega_D}{\pi T_c} \quad (22)$$

and formula (21) coincides with the results obtained by Shapoval[4].

In real superconductors the quantity $\mu(\partial \ln T_c/\partial\mu)$ can differ strongly from the model value (22). A correction of the order of $(p_0 d)^{-1}$ appears also in the right-hand side of (17) as a result of the change in the phonon spectrum. Comparing formulas (9) and (21) we see that the fluctuation shift T_c contains an additional small factor $(pl_{tr})^{-1}$ and can become larger than expression (21) only if the quantity $\mu(\partial \ln T_c/\partial\mu)$ is anomalously small in comparison with its value (22) as given by the BCS theory.

It follows from (12) and (21) that when the granule dimension or the transverse dimension of the filament is decreased, the region of the smearing of the phase transition becomes larger than the size-effect shift of T_c (formula (21)), if the condition

$$\left(\frac{3\pi^2 v}{2^{11}pRl_{tr}T}\right)^{1/3} > \left|\mu\frac{\partial \ln T_c}{\partial\mu}\right| \quad (23)$$

is satisfied for the filament and the condition

$$\left(\frac{v}{TR}\right)^{1/2} > \left|\mu\frac{\partial \ln T_c}{\partial\mu}\right|$$

for the granule.

Naugle and Glover obtained the dependence of the transition temperature on the thickness for amorphous Bi and Ge films. Using expression (4) for conductivity, we can represent the experimental results of[1] in the form

$$-\frac{\delta T_c}{T_c}=\frac{10\text{Å}}{d}=\frac{7.6}{p^2l_{tr}d}\ \text{for Bi,}$$
$$-\frac{\delta T_c}{T_c}=\frac{3.4\text{Å}}{d}=\frac{12}{p^2l_{tr}d}\ \text{for Ga.} \quad (24)$$

From (9) we obtain for the shift of T_c

$$-\frac{\delta T_c}{T_c}\approx\frac{1,3}{p^2l_{tr}d}\ln(p^2l_{tr}d)-\frac{0.25}{p^2l_{tr}d}\left[\ln\left(\frac{vl_{tr}}{d^2T}\right)\right]^3. \quad (25)$$

Substituting under the logarithm of (25) the mean value of the film thickness (10^3 and 3×10^3 Å for Bi and Ga, respectively), we obtain

$$-\frac{\delta T_c}{T_c}=\frac{8,6}{p^2l_{tr}d}-\frac{0.25}{p^2l_{tr}d}\left[\ln\left(\frac{vl_{tr}}{d^2T}\right)\right]^3\ \text{for Bi,}$$
$$-\frac{\delta T_c}{T_c}=\frac{12}{p^2l_{tr}d}-\frac{0.25}{p^2l_{tr}d}\left[\ln\left(\frac{vl_{tr}}{d^2T}\right)\right]^3\ \text{for Ga.} \quad (26)$$

If the second term is disregarded, expressions (24) and (26) are equal with good accuracy. Unfortunately, it is impossible to estimate the second term of (25), since we do not know the effective mass and the velocity on the Fermi surface.

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