Surface Dependent Geometrical Resonance of Superconductors

W. SCHATTKE

Institut für Theoretische Physik und Sternwarte der Universität Kiel

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The nonlocal integral equation obtained previously allows the determination of the amplitude of Geometrical Resonances in the McMillan-Anderson model. Surface conditions are defined by an adjustable parameter p which is fixed to fit the critical thickness measurements of the Proximity Effect.

A) Geometrical Resonance

In the tunneling characteristic dV/dJ of film diodes being composed of a thin and a relative thick superconducting film separated by an oxide layer (e. g. 300 Å and 3 μ thick, respectively, for an Al – Pb diode), as shown in Fig. 1, a periodic modulation of the usual tunneling characteristic can be observed the frequency of which depends strongly on the thickness d of the thick film [1]. The size of the thin film has no influence. The frequency is in the range

$$\frac{d}{2\pi\xi_0}\left(\xi_0=\frac{\hbar v_F}{\pi\varepsilon_0}\right),$$

where the parameters refer to quantities of the thick film. The amplitude of the oscillations is very small, so that the effect is detected more easily in the derivative d^2V/dJ^2 which exceeds dV/dJ by a factor d/ξ_0 (≈ 40 in the example mentioned above).

The effect is considerably enhanced by a normal-conducting metallic overlay covering the outer surface of the thick film [2].

The structure disappears, if the sample is warmed beyond the critical temperature of the thin film, even if the thick film remains superconducting.

For the theory of the effect it is supposed that the order parameter $\Delta(\boldsymbol{r})$ of the thick film is not constant and ε_0 in space.

A perturbation $\delta\Delta(\boldsymbol{r})$ of the order parameter at $\boldsymbol{r}$ alters the local density of states at any other point $\boldsymbol{r}'$ in an isotropic homogeneous superconductor.

$|\Delta(\boldsymbol{r})|^2$ stands roughly speaking for the density of the consended Cooper pairs. A change in $|\Delta(\boldsymbol{r})|$ means that single-particle excitations are scattered

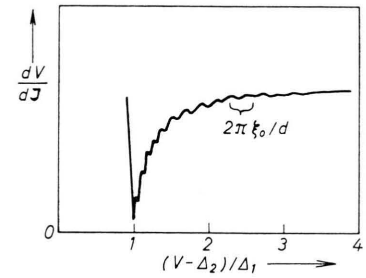

Fig. 1. $\Delta_1=\varepsilon_0$ and Δ_2, energy gap of the thick and thin film, respectively. Amplitude of the oscillations is exaggerated.

into and excited out of the Cooper sea by that perturbation. The original and the scattered states can combine to a new stationary state, if its energies are degenerate. Degeneration exists between the two states

$$|\boldsymbol{k}^+|=\sqrt{(2m/\hbar^2)(\zeta+\Omega)}\approx k_F+\Omega/(\hbar v_F), \quad (1)$$

$$|\boldsymbol{k}^-|=\sqrt{(2m/\hbar^2)(\zeta-\Omega)}\approx k_F-\Omega/(\hbar v_F) \quad (2)$$

where

$$\Omega=\sqrt{E^2-\varepsilon_0{}^2}, \quad (3)$$

$$E=E_{\boldsymbol{k}^+}=E_{\boldsymbol{k}^-}; \quad (4)$$

v_F, k_F are the absolute values of velocity and momentum at the Fermi level. Superposition of the two plane waves associated with $\boldsymbol{k}^+$ and $\boldsymbol{k}^-$ results in a local probability density at a distance d from the perturbation which is a periodic function of the argument $\frac{1}{2}(|\boldsymbol{k}^+|-|\boldsymbol{k}^-|)\,d=\Omega\,d/(\hbar v_F)$. The oscillations in the tunneling density of states are a consequence of that periodicity. The period does not depend on the strength of the perturbation, contrary to phase and amplitude which should show a dependence.

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[1] W. J. TOMASCH, Phys. Rev. Letters **15**, 672 [1965]. — W. J. TOMASCH and T. WOLFRAM, Phys. Rev. Letters **16**, 352 [1966]. — W. J. TOMASCH, Phys. Letters **26 A**, 379 [1968].

[2] W. J. TOMASCH, Phys. Rev. Letters **16**, 16 [1966].

A theoretical formulation of this phenomenon has been achieved by the McMillan-Anderson model [3], where the perturbation is assumed to be localized on the plane $x=d$. The ansatz is made

$$\delta \Delta(\boldsymbol{r}) = \delta \Delta \, \delta(x-d) . \qquad (5)$$

It results in a perturbation of the tunneling density of states which has been calculated at $x=0$ to lowest order in $\delta\Delta$. That result has been generalized by including all terms of higher order, i. e. the multiple scattering at the perturbation [4].

A model where the perturbation is spread over a certain range of the x-axis could be calculated exactly by solving Gorkov's equations for a superconducting system which is composed of two layers of different but constant order parameter [5].

B) Problem

The aim of this paper is to find out the dependence of the oscillations in the tunneling density of states on the surface condition of superconductors. The comparison with experiment cannot be complete, because the experimental data carry only few information concerning amplitude and phase of the oscillations. Boundary conditions have been obtained through a set of integral equations in a previous paper [6]. The solution of those equations gives the spatial variation of the order parameter and the value of the critical temperature. There appears a pair-breaking parameter p which stands for the probability that the incident Cooper pairs are broken by the surface. A normalconducting, metallic cover for instance shows strong pair-breaking. It can be used to determine the value of p by measuring the critical temperature of such a system.

If the deviation $(\Delta(\boldsymbol{r}) - \varepsilon_0)$ is put into the equation of the McMillan-Anderson model and it is integrated over space, the influence of the surface conditions on the Geometrical Resonances are obtained and the enhancement of the structure can be calculated.

For our purpose the McMillan-Anderson model is satisfactory, because the order parameter is evaluated from equations which are valid only under the assumption of $|\Delta(\boldsymbol{r}) - \int \Delta(\boldsymbol{r}) \, d^3\boldsymbol{r}|$ being small. Regarding that condition the theory thus will remain selfconsistent.

In the next section we shall determine the p-dependence of the order parameter. That is followed by the application to the McMillan-Anderson model in section D.

C) Order Parameter

The superconducting volume is assumed to be bounded by the planes

$$x = \pm d/2, \quad y = \pm L/2 \quad \text{and} \quad z = \pm L/2 .$$

Periodic boundary conditions with period L are chosen in the y- and z-direction. The surface $x = +d/2$ is pair-breaking, determined by the parameter p. On the opposite surface we have only diffuse scattering of the Cooper pairs. The free energy difference per unit area of the bulk material, i. e. with periodic boundary conditions in all directions, is given in I. It differs from the Ginzburg-Landau free energy in the nonlocal term on the right hand side of Eq. (6), which reduces in the local limit to the usual Ginzburg-Landau term.

$$m = -\frac{H_0^2}{4\pi\varepsilon_0^2} \int\limits_{-L/2}^{+L/2} dx \, (\Delta(x))^2 \left[1 - \frac{1}{2}\left(\frac{\Delta(x)}{\varepsilon_0}\right)^2\right] + \iint\limits_{-L/2}^{+L/2} dx \, dx' \, K(|x-x'|) \, \frac{d\Delta(x)}{dx} \, \frac{d\Delta(x')}{dx'} . \qquad (6)$$

Now we have to restrict the range of integration to the true superconducting volume $-d/2 \leqq x \leqq +d/2$. The integrand in the first term on the right hand side of Eq. (6) represents the free energy per unit volume which consequently has to be integrated only over the interval $[-d/2, +d/2]$.

[3] W. L. McMillan and P. W. Anderson, Phys. Rev. Letters **16**, 85 [1966].

[4] T. Wolfram and M. B. Einhorn, Phys. Rev. Letters **17**, 966 [1966].

[5] T. Wolfram, Phys. Rev. **170**, 481 [1968].

[6] W. Schattke, Z. Naturforsch. **23 a**, 1822 [1968], hereafter denoted as I.

In order to introduce boundary conditions into the second term in Eq. (6), we shall briefly discuss the results for the two essentially different mechanisms of surface scattering, as obtained in I.

1) A surface which is not pair-breaking can be characterized by the assumption, that the order parameter remains constant on the outside. This means, that in the part of the volume of periodicity which is outside the superconducting region, the derivative $\mathrm{d}\Delta(x)/\mathrm{d}x$ vanishes. In the present case this means, that the lower limit of integration can be shifted from $-L/2$ to $-d/2$, since the lower surface is assumed to be non-pairbreaking. If we would make the same assumption for the other surface, we would obtain

$$\iint\limits_{-d/2}^{+d/2} \mathrm{d}x\,\mathrm{d}x'\,K(|x-x'|)\,\frac{\mathrm{d}\Delta(x)}{\mathrm{d}x}\,\frac{\mathrm{d}\Delta(x')}{\mathrm{d}x'}\,. \tag{7}$$

2) A pair-breaking surface is supposed to break up the Cooper pairs ariving at the surface and to scatter them back as free particles. This is equivalent with the assumption, that $\Delta(x)\equiv 0$ outside the surface, i. e. in the part of the volume of periodicity which is not inside the superconductor. Since this implies, that $\mathrm{d}\Delta(x)/\mathrm{d}x$ is zero in the same region, the integration can be again restricted to the superconductor. However, the discontinuity of $\mathrm{d}\Delta(x)/\mathrm{d}x$ introduces some additional surface terms, so that the final result would be

$$\iint\limits_{-d/2}^{+d/2} \mathrm{d}x\,\mathrm{d}x'\,K(|x-x'|)\,\frac{\mathrm{d}\Delta(x)}{\mathrm{d}x}\,\frac{\mathrm{d}\Delta(x')}{x'} - 2\,\Delta\left(+\frac{d}{2}\right)\int\limits_{-d/2}^{+d/2}\mathrm{d}x\,K\left(\left|x-\frac{d}{2}\right|\right)\frac{\mathrm{d}\Delta(x)}{\mathrm{d}x} + K(0)\left(\Delta\left(+\frac{d}{2}\right)\right)^2. \tag{8}$$

If the outer surface is not completely pair-breaking, but breaks only a fraction p of the arriving pairs, we have to combine Eqs. (7) and (8) with weights $1-p$ and p, respectively.

$$\iint\limits_{-d/2}^{+d/2} \mathrm{d}x\,\mathrm{d}x'\,K(|x-x'|)\,\frac{\mathrm{d}\Delta(x)}{\mathrm{d}x}\,\frac{\mathrm{d}\Delta(x')}{\mathrm{d}x'} - 2\,p\,\Delta\left(+\frac{d}{2}\right)\int\limits_{-d/2}^{+d/2}\mathrm{d}x\,K\left(\left|x-\frac{d}{2}\right|\right)\frac{\mathrm{d}\Delta(x)}{\mathrm{d}x} + p\,K(0)\left(\Delta\left(+\frac{d}{2}\right)\right)^2. \tag{9}$$

$\Delta(x)$ is determined by the minimum of m. We shall find the minimum through its variational equations. The boundary values of $\Delta(x)$ will not be varied, because we are only interested in a continuous solution for $\Delta(x)$. Therefore we drop the third term in Eq. (9) and get for the free energy difference m, Eq. (6)

$$m = -\frac{H_0^2}{4\pi\,\varepsilon_0^2}\int\limits_{-d/2}^{+d/2}\mathrm{d}x\,(\Delta(x))^2\left[1-\frac{1}{2}\left(\frac{\Delta(x)}{\varepsilon_0}\right)^2\right] + \iint\limits_{-d/2}^{+d/2}\mathrm{d}x\,\mathrm{d}x'\,K(|x-x'|)\,\frac{\mathrm{d}\Delta(x)}{\mathrm{d}x}\,\frac{\mathrm{d}\Delta(x')}{\mathrm{d}x'}$$
$$-2\,p\,\Delta\left(+\frac{d}{2}\right)\int\limits_{-d/2}^{+d/2}\mathrm{d}x\,K\left(\left|x-\frac{d}{2}\right|\right)\frac{\mathrm{d}\Delta(x)}{\mathrm{d}x}\,. \tag{10}$$

The kernel $K(|x-x'|)$ is defined by the kernels $K_1(|x-x'|)$ and $K_3(|x-x'|)$ given in I according to

$$\frac{\partial^2}{\partial x^2}\,K(|x-x'|) = \frac{\hbar^2}{2\,m}\,\frac{\partial^2}{\partial x^2}\,K_1(|x-x'|) - 2\,\Delta^2\,K_3(|x-x'|) \tag{11}$$

and the condition, that $K(|x-x'|)$ must vanish for large distances. The coefficient $K(q)$ in the Fourier representation

$$K(|x-x'|) = \frac{1}{2\pi}\int\limits_{-\infty}^{+\infty}\mathrm{d}q\,K(q)\,e^{-iq(x-x')} \tag{12}$$

can be expanded in the neighbourhood of $|q|=0$ and $|q|=\infty$

$$K(q) = \frac{n\,\hbar^2\,\beta^2}{4\,m\,\pi^2}\left\{a^{\mathrm{II}}(\tau) + \tfrac{2}{3}\,\tau\,a^{\mathrm{III}}(\tau) + \tfrac{1}{10}\,(\beta\,q\,\xi_0\,\varepsilon_0)^2\left[a^{\mathrm{III}}(\tau) + \tfrac{2}{5}\,\tau\,a^{\mathrm{IV}}(\tau)\right]\right\}, \quad |q|\,\xi_0 \ll 1\,, \tag{13}$$

$$K(q) = \frac{3\,n\,\hbar^2}{2\,m\,(\pi\,q\,\xi_0\,\varepsilon_0)^2}\left\{\log\frac{\pi\,|q|\,\xi_0}{e\,t} - a^{\mathrm{I}}(\tau) - 2\,\tau\,a^{\mathrm{II}}(\tau)\right\}, \quad |q|\,\xi_0 \gg 1 \tag{14}$$

where

$$a(\tau) = 2 \sum_{l=1} \left(\frac{\tau}{l} + 2\,l - 2\sqrt{l^2+\tau} \right), \tag{15}$$

$$l = 1, 3, 5, \ldots, \ (\text{s.}\ ^7),$$

$$\Delta = \frac{1}{d} \int_{-d/2}^{+d/2} \mathrm{d}x\, \Delta(x). \tag{16}$$

n is the electron density, $t = T/T_c$ the reduced temperature

$$\left(\beta = \frac{1}{k\,T},\quad \tau = \left(\frac{\beta\,\Delta}{\pi}\right)^2\right).$$

For the sake of simplicity we shall interpolate between both expressions, Eqs. (13) and (14), to get for the kernel a rational fraction. From an exact representation which may be derived by contour integration from the corresponding formula in I, we find some properties which the approximate kernel $K_a(|x-x'|)$ must display.

$$K(|x-x'|) = \frac{3\,n\,\xi_0\,\varepsilon_0\,\beta}{8\,\zeta} \sum_{l=1} \frac{l^2}{c_l^4}\, E_3\left(\frac{2\,|x-x'|}{\xi_0\,\varepsilon_0\,\beta}\, c_l\right),$$

$$l = 1, 3, 5, \ldots, \tag{17}$$

$c_l = \sqrt{l^2+\tau}$, $E_3(z)$ Exponential integral [8].
As a consequence we have to approximate $K(q)$ in such a way that $K_a(z)$ is a positive, bounded, monotonic decreasing function of z which vanishes for large z at least like an exponential function.

An approximation which satisfies Eqs. (13) and (14) is

$$K_a(q) = \alpha_1 \left\{1 + \frac{\alpha_2\, q^2}{\log(\beta_1 + \beta_2\,|q|)}\right\}^{-1} \tag{18}$$

where

$$\alpha_1 = \frac{n\,\hbar^2\,\beta^2}{4\,m\,\pi^2}\,[a^{\mathrm{II}}(\tau) + \tfrac{2}{3}\,\tau\, a^{\mathrm{III}}(\tau)] \Rightarrow \frac{n\,\hbar^2}{24\,m\,\Delta^2}, \tag{19 a}$$

$$\alpha_2 = \frac{2\,m\,\pi^2\,\varepsilon_0^2\,\xi_0^2}{3\,n\,\hbar^2}\,\alpha_1 \Rightarrow \left(\frac{\pi\,\varepsilon_0\,\xi_0}{6\,\Delta}\right)^2, \tag{19 b}$$

$$\log\beta_1 = -\frac{5}{3}\,\frac{[a^{\mathrm{II}}(\tau) + \frac{2}{3}\,\tau\,a^{\mathrm{III}}(\tau)]^2}{a^{\mathrm{III}}(\tau) + \frac{2}{5}\,\tau\,a^{\mathrm{IV}}(\tau)} \Rightarrow \frac{25}{54}, \tag{19 c}$$

$$\log\beta_2\,|q| = \log\frac{\pi\,|q|\,\xi_0}{e\,t} - a^{\mathrm{I}}(\tau) - 2\,\tau\,a^{\mathrm{II}}(\tau)$$

$$\Rightarrow \log\left(\frac{\pi\,|q|\,\xi_0\,\varepsilon_0}{e^2\,\Delta}\right). \tag{19 d}$$

The limiting values in the expressions above refer to $T = 0\ ^\circ\mathrm{K}$. At the critical temperature of the film Eq. (18) must coincide with a formula mentioned earlier, Eq. (49) in I. Accordingly $|q|$ in $\log(\beta_1 + \beta_2\,|q|)$ has to be replaced by $e/(\gamma\,d)$. Thus the kernel may be written

$$K_a(|x-x'|) = \alpha \exp\left\{-\frac{1}{\xi}\,|x-x'|\right\} \tag{20}$$

$$\alpha = \tfrac{1}{2}\,\alpha_1\,\alpha_2^{-1/2}\left[\log\left(\beta_1 + \beta_2\,\frac{e}{\gamma\,d}\right)\right]^{1/2} \approx \tfrac{1}{2}\,\alpha_1\,\alpha_2^{-1/2}, \tag{21 a}$$

$$\xi = \frac{\alpha_1}{2\,\alpha} \approx \alpha_2^{1/2} \tag{21 b}$$

where the given approximations are valid for $d \gtrsim 30\,\xi_0$, which covers the thickness range of the measured samples.

Since the deviation of the order parameter from its average is small, the variational equation of Eq. (10) may be linearized retaining terms in Eq. (10) only up to second order in $\psi(x)$.

$$\Delta(x) = \Delta(1 + \psi(x)), \tag{22}$$

$$\int_{-d/2}^{+d/2} \mathrm{d}x\,\psi(x) = 0. \tag{23}$$

The condition in Eq. (23) is satisfied by a Lagrangian parameter η. We get the variational equation

$$\begin{aligned} 0 = A_0 &+ \left[p - (1-p)\,\psi\left(+\frac{d}{2}\right)\right] \exp\left\{-\frac{1}{\xi}\left(\frac{d}{2} - x\right)\right\} \\ &- \psi\left(-\frac{d}{2}\right)\exp\left\{-\frac{1}{\xi}\left(\frac{d}{2} + x\right)\right\} + A_1\,\psi(x) \\ &- \frac{1}{\xi}\int_{-d/2}^{+d/2} \mathrm{d}x'\,\exp\left\{-\frac{1}{\xi}\,|x-x'|\right\}\psi(x'), \end{aligned} \tag{24}$$

$$A_0 = \frac{\xi\,\eta}{2\,\Delta\,\alpha} - \frac{H_0^2\,\xi}{4\,\pi\,\varepsilon_0^2\,\alpha}\left(1 - \frac{\Delta^2}{\varepsilon_0^2}\right), \tag{25}$$

$$A_1 = 2 - \frac{H_0^2\,\xi}{4\,\pi\,\varepsilon_0^2\,\alpha}\left(1 - 3\,\frac{\Delta^2}{\varepsilon_0^2}\right). \tag{26}$$

The solution to Eq. (24) is easily obtained

$$\psi(x) = \frac{A_0}{2-A_1} - p\left(1 + \frac{A_0}{2-A_1}\right)\frac{1-\varrho\,\xi}{1-(1-p)\,(1-\varrho\,\xi)} \cdot \exp\left\{\varrho\left(x - \frac{d}{2}\right)\right\}, \tag{27}$$

$$\varrho = \frac{1}{\xi}\sqrt{\frac{A_1-2}{A_1}}. \tag{28}$$

Thus the order parameter may be regarded as constant in space up to a small distance $1/\varrho$ from the pair-breaking surface (Fig. 2). Terms of order $e^{-\varrho d}$ have been dropped. η, Eq. (25), is determined by Eq. (23). That variational condition meant that the

[7] B. MÜHLSCHLEGEL, Z. Phys. **155**, 313 [1959].

[8] Handbook of Mathematical Functions, ed. by M. ABRAMOWITZ and J. A. STEGUN, NBS [1964].

mean value Δ should be held constant. After solving Eq. (24) for $\psi(x)$ and putting this in Eq. (10) we now can determine Δ from the minimum of Eq. (10). We omit some simple but tedious calculations. Δ is given by

$$\left(\frac{\Delta}{\varepsilon_0}\right)^2 = 1 - \frac{p^2\,\xi_0}{d}\,a\,, \quad 0 < a \lesssim \frac{1}{10} \tag{29}$$

if $d \gtrsim 30\,\xi_0$. The result is not surprising and we may set as a consequence in all formulas $\Delta = \varepsilon_0$. $A_0/(2-A_1)$ in Eq. (27) is small to unity and can be neglected. Eq. (27) is put into Eq. (22) and we get

$$\Delta(x) = \varepsilon_0\left(1 - c\,\exp\left\{\varrho\left(x - \frac{d}{2}\right)\right\}\right) \tag{30}$$

$$c = \frac{p\,(1-\varrho\,\xi)}{1-(1-p)\,(1-\varrho\,\xi)}\,, \tag{31}$$

and from Eqs. (19 a, b), (21 a, b), (26) and (28) the numerical quantities

$$\varrho\,\xi = \sqrt{\frac{2}{3}}\,, \quad \varrho\,\xi_0 = \frac{2}{\pi}\sqrt{6}\,. \tag{32 a, b}$$

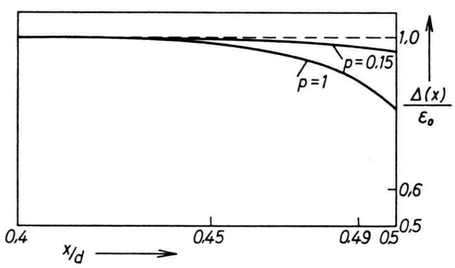

Fig. 2. Spatial dependence of the order parameter $\Delta(x)$ ($d=30\,\xi_0$, $x=d/2$ pair-breaking surface).

The only unknown quantity in Eq. (30) is the parameter p which we shall relate to the critical thickness D_{s0} of the Proximity effect [9]. A thin film does not exhibit superconductivity as a consequence of its surface properties, if d becomes smaller than a thereby defined critical thickness D_{s0}.

By Eqs. (54) and (55) of I a function $T_c'(d/\xi_0)/T_c$ is defined the first derivative of which becomes positive infinite at a certain point d_0/ξ_0. T_c' and T_c are the critical temperatures of the film and the bulk, respectively. Above d_0 the function $T_c'(d)$ is monotonic increasing with the asymptotic value

$$T_c'(\infty) = T_c\,.$$

As a function of p we can approximate d_0/ξ_0 by

$$\frac{d_0}{\xi_0} = \frac{1.76}{p}\,(1+1.7\,p)\,\exp\left\{-\frac{1}{p}\right\} \tag{33}$$

[9] P. Hilsch and R. Hilsch, Z. Phys. **180**, 10 [1964].

for $0 \leqq p \leqq 0.5$ (Fig. 3). The curves in Fig. 1 of I are not extended up to that point, because it does not belong to the second order phase transition presumed in the derivation. Nevertheless we shall identify both quantities

$$d_0 = D_{s0} \tag{34}$$

because that is one possibility to fit the measurements of Proximity effect satisfactorily with the theoretical curves of I. Aside from that practical use d_0 has no real meaning.

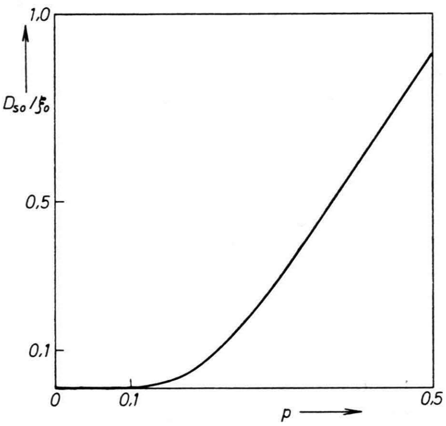

Fig. 3. Normalized critical thickness D_{s0}/ξ_0 vs. surface parameter p.

D) Tunneling Density of States

The main idea of the McMillan-Anderson model consists in the assumption of a local perturbation of the order parameter, Eq. (5), in a homogeneous, isotropic superconductor. The periodic modulation of the tunneling density of states is then already established by first order perturbation calculation. On account of that linearity we can calculate the effect of the perturbation given in Eq. (30) by simple integration of the result of McMillan and Anderson. For clarity we cite their formulas.

$G_\omega^{(1)}(\boldsymbol{r}, \boldsymbol{r}')$ is the resulting perturbation of the Fourier transformed Green's function $G_\omega^{(0)}(|\boldsymbol{r}-\boldsymbol{r}'|)$, if the constant order parameter ε_0 is perturbed by an amount $\delta\Delta(\boldsymbol{r})$, Eq. (30). From Gorkov's equations we get

$$G_\omega^{(1)}(\boldsymbol{r}, \boldsymbol{r}') = \frac{1}{\hbar}\int_{\mathrm{SL}} \mathrm{d}^3\boldsymbol{r}_1 \{G_\omega^{(0)}(|\boldsymbol{r}-\boldsymbol{r}_1|)\,\delta\Delta(\boldsymbol{r}_1)\,F_\omega^{+(0)}(|\boldsymbol{r}_1-\boldsymbol{r}'|) + F_\omega^{+(0)}(|\boldsymbol{r}-\boldsymbol{r}_1|)\,\delta\Delta(\boldsymbol{r}_1)\,G_\omega^{(0)}(|\boldsymbol{r}_1-\boldsymbol{r}'|)\} \tag{35}$$

where the unperturbed Green's functions are

$$G_\omega^{(0)}(R) \qquad (36)$$

$$= -\frac{m}{4\pi\hbar R}\left[\left(1-\frac{\hbar\omega}{\Omega}\right)\exp\left\{-iR\left|\frac{2m}{\hbar^2}(\mu-\Omega)\right|^{1/2}\right\} + \left(1+\frac{\hbar\omega}{\Omega}\right)\exp\left\{+iR\left|\frac{2m}{\hbar^2}(\mu+\Omega)\right|^{1/2}\right\}\right]$$

$$F_\omega^{+(0)}(R) = \frac{m\,\varepsilon_0}{4\pi\hbar R\,\Omega}\left[\exp\left\{-iR\left|\frac{2m}{\hbar^2}(\mu-\Omega)\right|^{1/2}\right\} - \exp\left\{+iR\left|\frac{2m}{\hbar^2}(\mu+\Omega)\right|^{1/2}\right\}\right] \qquad (37)$$

for $0<\Omega<\mu$.

$$\Omega = \left|(\hbar\omega)^2-\varepsilon_0^2\right|^{1/2}. \qquad (38)$$

The integration in Eq. (35) runs over the superconducting volume. The local density of states $N_\omega(\boldsymbol{r})$ of one spin at $\boldsymbol{r}$ is

$$N_\omega(\boldsymbol{r}) = -\frac{1}{\pi\hbar}\,\mathrm{Im}\,G_\omega(\boldsymbol{r},\boldsymbol{r}), \quad \omega \geqq 0 \qquad (39)$$

and

$$G_\omega(\boldsymbol{r},\boldsymbol{r}') = G_\omega^{(0)}(|\boldsymbol{r}-\boldsymbol{r}'|) + G_\omega^{(1)}(\boldsymbol{r},\boldsymbol{r}') \qquad (40)$$

where the energy $\hbar\omega$ has been taken relative to the Fermi energy ζ. We combine Eqs. (30), (31), (36) and (37) with Eq. (35) and perform two integrations of the threedimensional integral.

We get for $N_\omega(\boldsymbol{r})$ at the plane $x=-d/2$, Eq. (39),

$$N_\omega\left(x=-\frac{d}{2}\right) \qquad (41)$$

$$= N_0\,\frac{\hbar\omega}{\Omega}\left\{1-\frac{c\,\varepsilon_0}{\pi\,\varrho\,\xi_0\,\Omega}\,f\left(\frac{2\,d\,\Omega}{\pi\,\xi_0\,\varepsilon_0},\,\varrho\,d\right)\right\},$$

$$= N_0\,\frac{\hbar\omega}{\Omega}\left\{1-\frac{0.04\,p}{1+0.2\,p}\,\frac{\varepsilon_0}{\Omega}\,f\left(\frac{2\,d\,\Omega}{\pi\,\xi_0\,\varepsilon_0},\,\frac{2\sqrt{3}\,d}{\pi\,\xi_0}\right)\right\} \qquad (42)$$

where we used Eqs. (32 a) and (32 b). The function f is defined by

$$f(x,y) = \mathrm{si}(x) - \int_0^1 \frac{\mathrm{d}t}{t}\,e^{y(t-1)}\sin(x\,t) \qquad (43)$$

$\mathrm{si}(x)$ = Sine integral [8].

N_0 is the density of states of the free electron gas at the Fermi level. To get Eq. (41) we neglected quantities of order $O(1/k_F\,\xi_0)$ relative to unity. As a consequence the rapidly oscillating terms could be dropped. Only the term which represents the interference of two waves of comparable wavelength survived. The function defined in Eq. (43) can be approximated for $y \gtrsim 30$;

$$f(x,y) \approx \mathrm{si}(x) + \frac{x\cos x - y\sin x}{x^2+y^2}. \qquad (44)$$

The shape of $f(x,y)$ is shown in Fig. 4 exhibiting the oscillations of the density of states.

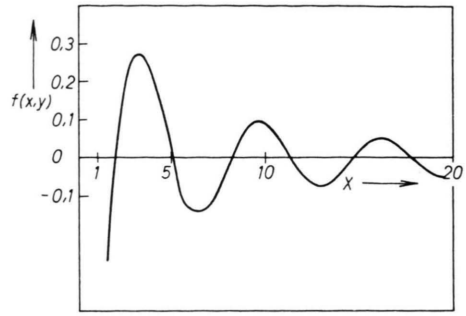

Fig. 4. For definition of $f(x,y)$ s. text ($y=30$).

The discussion of the result is limited because there are only few experimental data available. We shall investigate two cases, p being small and of order unity, respectively.

First we consider the case of superconducting films prepared without a metallic overlay, i. e. small p. Along the results of STRONGIN et al. [10] and OPITZ [11] we find $D_{s0}\approx 30$ Å, $D_{s0}/\xi_0=0.04$ for Pb and $D_{s0}\approx 45$ Å, $D_{s0}/\xi_0\approx 0.01$ for In, respectively *. The appropriate value of p is $p\approx 0.15$ for Pb and ≈ 0.13 for In, Fig. 3. Thus the numerical factor on the right hand side of Eq. (42) which determines the strength of the oscillations is ≈ 0.006 and ≈ 0.005, respectively.

On the other hand for $p=1$ we find that factor to be ≈ 0.033, about six times the value for small p. That agrees to some extent with the experimental data of TOMASCH [2]. The comparison can only give a rough approximation of the true facts, because the samples are prepared by the different authors most likely in a different way. The greatest value $p=1$ should be approximately realized in the used films covered with an Ag-overlay of 2000 Å.

To relate the absolute value of the oscillations in the density of states with the first derivative of the tunneling characteristic we have to calculate

$$\frac{\mathrm{d}J_{\mathrm{osc}}}{\mathrm{d}V} \sim \frac{\mathrm{d}}{\mathrm{d}V}\left\{\int_{\varepsilon_0}^{\mathrm{eV}-\Delta_2}\delta N_1(E)\,N_2(\mathrm{eV}-E)\,\mathrm{d}E\right\} \qquad (45)$$

[10] M. STRONGIN and O. F. KAMMERER, J. Appl. Phys. **39**, 2509 [1968].

[11] W. OPITZ, Z. Phys. **141**, 263 [1955].

* A review of critical temperature measurements on films of various superconductors is given in W. KESSEL and W. RÜHL, PTB-Mitteilungen **79**, 258 [1969].

where $N_2(E)$ is the tunneling density of states of the thin film, i. e. that part of the diode which is not responsible for the Geometrical Resonance. If the thin film consists of a normalconducting metal, i. e. $\Delta_2 \equiv 0$, we can just set

$$\mathrm{d}J_{\mathrm{osc}}/\mathrm{d}V \sim N_0\,\delta N_1(\mathrm{eV}) \qquad (46)$$

where N_0 is the density of states of the normal metal. If the thin film is a superconductor we have to evaluate the integral in Eq. (45). There seems to be an enhancement in the periodic structure when the thin film becomes superconducting because of the energy gap singularity in the density of states. In this case many electrons are available in a relative small energy interval to tunnel from the thin film into the thick film, into states of rapidly varying density. The right hand side of Eq. (45) can be estimated. As a result the ratio of the oscillation amplitude in Eq. (45) to the amplitude in Eq. (46) varies for $d/\xi_0 \gg 1$ like $(d\,\Delta_2/\xi_0\,\varepsilon_0)$. A numerical calculation leads to ≈ 5 for that ratio at the special values $d/\xi_0 = 30$, $\Delta_2/\xi_0 = 1/3$, $\mathrm{eV}/\varepsilon_0 \gtrsim 2$, i. e. the phase change to the normal state in the thin film would reduce the structure in that case by a factor 1/5. Thus a thick film without overlay connected with a superconducting thin film should have an oscillating part of $\approx 1\%$ at the first maximum in the first derivative of the tunneling characteristic.

It should be emphasized, that the results of this section are no longer valid, if the tunneling energy $\hbar\,\omega$ is near the energy gap ε_0. That is a consequence of the perturbation calculation used in the McMillan-Anderson model. It follows that a quantitative comparison has to be restricted to values of eV beyond the range of the strong increase in $\mathrm{d}V/\mathrm{d}J$ near ε_0.

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