ELECTRON SPECTRUM OF THE INTERMEDIATE STATE OF SUPERCONDUCTORS

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It is shown that at energies of the order of v/a (v is the Fermi velocity, a the thickness of the normal layers) quantization of the energy levels of electron excitations becomes important. As a result, the temperature dependence of the thermodynamic quantities changes at temperatures of the order of 0.1°K.

THE intermediate state of a superconductor is a system of alternating layers of normal and superconducting phases.[1] It occurs when a superconductor of finite dimensions is placed in an external magnetic field in the range from $H_c(1-n)$ to H_c (n is the demagnetization factor, H_c is the critical magnetic field).

Let us consider the problem of the spectrum of electron excitations with energies that are small in comparison with the critical temperature of the superconducting transition in the absence of a magnetic field. It is evident from the very beginning that such excitations must be localized in normal regions, inasmuch as there is an energy gap Δ in the superconducting layers of the same order of magnitude as T_c.

The nontriviality of the stated problem is associated with the following circumstance, which is significant in the rest of the work. The ordinary excitations ("electrons" and "holes") of an infinite, normal metal (the spectrum of which has the form $\epsilon = |\xi(p)|$, where ϵ is the energy, $\mathbf{p}$ the momentum, $\xi = v(p-p_0)$; v and p_0 are the velocity and momentum on the Fermi surface) cannot penetrate in the superconducting region, since it is assumed that $\epsilon \ll \Delta$. On the phase separation boundary the excitations must consequently undergo reflection. As has been shown earlier,[2] this reflection has a number of specific characteristics.

The point is that the momentum of the excitations can have a value close to p_0. On the other hand, the width of the transition layer between phases, that is, the distance at which the energy gap changes from zero in the normal phase to a value of the order of T_c in the superconducting phase, is equal to the coherence parameter $\xi_0 \sim 10^{-4}$ cm. The corresponding uncertainty of the momentum of the excitation $\Delta p \sim 1/\xi_0$ is much less than p_0. The ratio of the "potential energy" $\Delta(\mathbf{r})$ to the Fermi energy is also small. Thus the inhomogeneity in the transition layer is too weak for ordinary reflection processes, i.e., processes as a result of which the excitation momentum changes by a quantity of the order of p_0, to take place with significant probability. There exists another reflection mechanism which is peculiar to this problem, as the result of which the excitation momentum $\mathbf{p}$ is practically unchanged (see [2]). Here, however, the "electron," that is, an excitation with $\xi > 0$, undergoes a transition to a "hole" ($\xi < 0$), and vice versa. For this reason, all three components of the velocity $\mathbf{v} = \partial\epsilon/\partial\mathbf{p}$ change sign.

It is easy to see that as a result of such a reflection from both boundaries of the normal layer, the excitation will carry out periodic motions in which it will be an "electron" during one half period and a "hole" during the other. In other words, standing waves will arise in the normal layer and lead to a quantization of the excitation energy levels. It is very important that this quantization becomes significant at values of the thickness of the normal layers $a \sim 1/|p-p_0|$ (and not when $a \sim 1/p_0$). This is directly connected with the fact that the excitation momentum $\mathbf{p}$ is practically unchanged in reflection.

Since $|p-p_0| \sim \epsilon/v$, the quantization of the levels becomes important at energies $\epsilon \sim v/a$. Excitations with such energies make the main contribution to the thermodynamic quantities at temperatures $T \sim v/a$. If we substitute the typical values $v \sim 10^8$ cm/sec, $a \sim 10^{-2}$ cm, then we get a temperature of the order of 0.1°K, which is quite accessible to experiment.

The form of the spectrum of the low-lying energy levels of the electron excitations will be found below, and it will be shown that the quantization of these levels furnishes significant information on the thermodynamic and other properties of the intermediate state.

1. We assume that the mean free path of the electrons and the Larmor radius in a magnetic field, equal to the critical field at absolute zero, significantly exceed the thickness of the normal layers. (This was essentially assumed by us in the discussions carried out above.) Then, to find the energy levels ϵ, one must start out from the equations for the wave functions of the excitation (see [2]):

$$\left[i\mathbf{v}\left(\frac{\partial}{\partial\mathbf{r}} - ie\mathbf{A}\right) + \varepsilon\right]\eta + i\Delta(\mathbf{r})\chi = 0,$$
$$\left[i\mathbf{v}\left(\frac{\partial}{\partial\mathbf{r}} + ie\mathbf{A}\right) - \varepsilon\right]\chi + i\Delta^*(\mathbf{r})\eta = 0, \qquad (1)$$

where $\mathbf{v} = v\mathbf{n}$, $\mathbf{n}$ is a unit vector along the direction of the excitation momentum, $\mathbf{A}$ is the vector potential, $\Delta(\mathbf{r})$ is the energy gap, and e is the electron charge. We choose a system of coordinates such that the z axis is normal to the boundary separating the phases while the plane $z = 0$ lies in the middle of the normal layer. From symmetry considerations it is evident that $|\Delta(\mathbf{r})|$ depends only on the z coordinate, so that Δ has the form $F(z)e^{i\varphi(\mathbf{r})}$. Inasmuch as $\varphi(\mathbf{r})$ can be made equal to zero by means of a gauge transformation, the gap Δ can be considered to be real and dependent only on z.

In the region $-a/2 < z < a/2$ (a is the thickness of the normal layer), occupied by the normal phase, $\Delta(z)$ is practically equal to zero and the set (1) is materially simplified:

$$\left[i\mathbf{v}\left(\frac{\partial}{\partial\mathbf{r}} - ie\mathbf{A}\right) + \varepsilon\right]\eta = 0,$$
$$\left[i\mathbf{v}\left(\frac{\partial}{\partial\mathbf{r}} + ie\mathbf{A}\right) - \varepsilon\right]\chi = 0. \qquad (2)$$

In the regions $z > a/2$ and $z < -a/2$ occupied by the superconducting phase, $\Delta(z)$ is equal to the equilibrium value Δ_0 and the system (1) has two solutions for $\epsilon < \Delta_0$, one of which decreases exponentially with depth in the superconducting phase, and the other increases exponentially.

We are interested in values of ϵ that are small in comparison with Δ_0. In this case, the excitation is localized essentially in the normal layer and the corresponding solutions of the set (1) must decay with depth in the superconducting phase. It is clear that to find such solutions it is necessary to solve the set (2) with boundary conditions for $z = a/2$ and $z = -a/2$, which would guarantee "matching" with the decaying solutions in the superconducting phase. Since (1) is a linear homogeneous set of equations of first order, the most general form of these boundary conditions is the following:

$$\eta = C_+\chi \quad \text{for} \quad z = a/2,$$
$$\eta = C_-\chi \quad \text{for} \quad z = -a/2, \qquad (3)$$

where C_+ and C_- are generally functions of the vector $\mathbf{n}$. It is essential that when $\epsilon \ll \Delta_0$ these can be assumed to be independent of the energy ϵ.

Let $\epsilon_0(\mathbf{n})$ be a certain energy level. This means that there exist functions $\eta_0(\mathbf{r})$ and $\chi_0(\mathbf{r})$ which satisfy (2) for $\epsilon = \epsilon_0$ and (3). We shall seek a solution of (2) and (3) in the form $\eta = \eta_0\eta'$ and $\chi = \chi_0\chi'$. Substituting these in (2) and (3), we get

$$i\mathbf{v}\frac{\partial\eta'}{\partial\mathbf{r}} + (\varepsilon - \varepsilon_0)\eta' = 0, \qquad i\mathbf{v}\frac{\partial\chi'}{\partial\mathbf{r}} - (\varepsilon - \varepsilon_0)\chi' = 0, \qquad (4)$$

where

$$\eta' = \chi' \quad \text{for} \quad z = \pm a/2. \qquad (5)$$

Equations (4) have the following solutions:

$$\eta' = Ae^{i\mathbf{q}_1\mathbf{r}}, \quad \chi' = Be^{i\mathbf{q}_2\mathbf{r}}; \qquad = \frac{[(\varepsilon - \varepsilon_0)]}{v}\mathbf{n}, \qquad (6)$$

$$\mathbf{q}_2\mathbf{n} = -\frac{\varepsilon - \varepsilon_0}{v}, \quad q_{2x} = q_{1x}, \quad q_{2y} = q_{1y}, \qquad (7)$$

where A and B are arbitrary constants.

Substituting (6) in (5), and setting the determinant of the resultant system of equations for A and B equal to zero, we have, with account of (7):

$$\sin\left\{\frac{\varepsilon - \varepsilon_0}{vn_z}a\right\} = 0, \qquad (8)$$

whence

$$\varepsilon = \varepsilon_0 + \pi vn_z m / a, \qquad (9)$$

where m is an integer. The last formula can now be rewritten in the form

$$\varepsilon_k(\mathbf{n}) = \pi v|n_z|(k + \gamma) / a, \qquad (10)$$

where $k = 0, 1, 2, \ldots$, and γ is some function of $\mathbf{n}$ such that $0 < \gamma < 1$.

We see that the energy of the excitation can take on a series of equivalent values while the distance between the levels is proportional to $|n_z|$. The latter circumstance is quite natural, since the excitation traverses the distance from one boundary of the normal layer to the other, equal to $a/|n_z|$.

2. Let us proceed to a calculation of the thermodynamic quantities. For this, it suffices to find an expression for the free energy of the normal layer, which is determined by the well-known relation

$$F = F_0 - T\sum_s \ln(1 + e^{-\varepsilon_s/T}) \qquad (11)$$

(F_0 is the free energy at absolute zero, while the summation is carried out over all states of the excitation). These states are determined by specifying the vector **n** and the integer k (for a given spin projection).

We shall find the number of levels with a given k per element of solid angle do_r. For this purpose, we note that the vector **n** is uniquely determined by specifying the momentum projections p_x and p_y: $n_x = p_x/p_0$, $n_y = p_y/p_0$. The number of states in the interval between p_x, p_y and $p_x + dp_x$, $p_y + dp_y$ is equal to $2S dp_x dp_y/(2\pi)^2$, where S is the area of the normal layer, the factor 2 being connected with summation over the spin. The latter expression can be rewritten in the following fashion:

$$2S\frac{dp_x\,dp_y}{(2\pi)^2}=2S\frac{p_t\,dp_t\,d\varphi}{(2\pi)^2}=2S\frac{p_0^2}{(2\pi)^2}\,|n_z|\,dn_z\,d\varphi;$$

$$p_t=\sqrt{p_x^2+p_y^2},\qquad \cos\varphi=p_x/p_t.$$

We have used the relation $p_t^2 = p_0^2(1 - n_z^2)$, whence it follows that $p_t dp_t = p_0^2 |n_z| dn_z$. The product $dn_z d\varphi$ is equal to the element of solid angle do_n, so that the desired number of level is equal to

$$2(2\pi)^{-2}Sp_0^2|n_z|\,do_{\mathbf{n}}.$$

Formula (11) for the free energy thus takes the form

$$F=F_0-\frac{Sp_0^2T}{2\pi^2}\sum_{k=0}^{\infty}\int do_{\mathbf{n}}\,|n_z|\ln\Big[1+\exp\Big(-\frac{\varepsilon_k(\mathbf{n})}{T}\Big)\Big],\qquad(12)$$

where $\epsilon_k(n)$ is determined by Eq. (10).

If the temperature $T \gg v/a$, then the summation over k can be replaced by integration, and we get the usual formula for the free energy of the layer

$$F=F_0-p_0^2T^2Sa\,/\,6v.\qquad(13)$$

We now consider the inverse limiting case of low temperatures, $T \ll v/a$. The principal contribution to the integral (12) is made by the region of small $|n_z|$, of the order Ta/v, in which the slowly changing function γ can be regarded as constant. Integration over n_z can be extended from $-\infty$ to $+\infty$:

$$F=F_0-\frac{Sp_0^2T}{\pi^2}\sum_{k=0}^{\infty}\int_0^{2\pi}d\varphi\times\int_0^{\infty}n_z\,dn_z\ln\Big\{1+\exp\Big[-\frac{\pi v n_z}{Ta}(k+\gamma)\Big]\Big\}.\qquad(14)$$

By means of simple transformations, the latter expression can be reduced to the form

$$F=F_0-\alpha S(p_0a\,/\,v)^2T^3,\qquad(15)$$

where α is a constant of the order of unity:

$$\alpha=\frac{3\zeta(3)}{4\pi^4}\sum_k\int_0^{2\pi}\frac{d\varphi}{(k+\gamma)^2}$$

$\zeta(x)$ is the Riemann zeta function. Formula (15) shows that the value of $F - F_0$ at low temperatures is proportional to the cube of the temperature and the square of the thickness of the normal layer a.

The foregoing formulas pertained to a single layer of normal phase. With their help, one can find the thermodynamic quantities pertaining to the intermediate state as a whole. For this purpose it is first necessary to compute the value of the magnetic field H_n in the normal phase. The latter is determined by the condition

$$H_{c0}^2\,/\,8\pi=H_n^2\,/\,8\pi-S^{-1}\partial(F-F_0)\,/\,\partial a,\qquad(16)$$

which follows from the equality of the normal forces on both sides of the boundary between phases (H_{c0} is the critical field at $T = 0$).

For $T \gg v/a$, we get from (16), with the aid of (13)

$$H_n^2\,/\,8\pi=H_{c0}^2\,/\,8\pi-p_0^2T^2\,/\,6v,\qquad(17)$$

which is identical with the expression for $H_c(T)$ for $T \ll T_c$ (see [3]).

For $T \ll v/a$, we have

$$H_n^2\,/\,8\pi=H_{c0}^2\,/\,8\pi-2\alpha(p_0\,/\,v)^2T^3a.\qquad(18)$$

The total free energy per unit volume of the intermediate state $\mathscr{F}$ is made up of two parts. The first comes from the free energy of the normal layers (the energy of the superconducting layers is exponentially small in the considered region of temperature $T \ll T_c$) and the second from the energy of the system in the external field H. The first of these is equal to $F/S(a+b)$, where b is the thickness of the superconducting layer; the second is equal to $MH/2$, where M is the magnetic moment per unit volume due to the currents flowing close to the boundaries between the phases. Its value is connected by a simple relation with the field H_n and with the concentration of the superconducting phase $x_s = b/(a+b)$ (cf. [4]):

$$M=H_nx_s\,/\,4\pi.\qquad(19)$$

The value of x_s is determined by the usual formula (see [4]), in which we replace H_c by H_n:

$$x_s=n^{-1}(1-H\,/\,H_n),\qquad(20)$$

where n is the demagnetization factor.[1)]

[1)]We are considering a superconductor of ellipsoidal form in an external field parallel to one of its axes.

Taking all the foregoing into account, and also the fact that the second terms in the right hand side of (17) and (18) are small in comparison with the first, and that the value of F_0 in (12)—(15) is equal to $SaH_{c0}^2/8\pi$, we get

$$\mathcal{F} = \mathcal{F}_0(H) + (F - F_0) / S(a + b), \qquad (21)$$

where $\mathcal{F}_0(H)$ is the value of $\mathcal{F}$ at $T = 0$.

From (21), with account of (13) and (15), one can easily obtain by simple differentiation the formulas for the specific heat per unit volume of the intermediate state at a given H:

$$C = \frac{p_0^2}{3v}\frac{a}{a+b}T \qquad (22)$$

for $T \gg v/a$, and

$$C = \frac{6\alpha}{a+b}\left(\frac{p_0 a}{v}\right)^2 T^2 \qquad (23)$$

for $T \ll v/a$.

We also write down the expressions for the magnetic moment, obtained from (19) in both limiting cases:

$$M = M_0(H) - \frac{p_0^2}{6nH_{c0}v}T^2, \quad T \gg v/a, \qquad (24)$$

$$M = M_0(H) - \frac{2\alpha a}{nH_{c0}}\left(\frac{p_0}{v}\right)^2 T^3, \quad T \ll v/a. \qquad (25)$$

Here M_0 is the magnetic moment at zero temperature.

As is seen from a comparision of (22) with (23) and (24) with (25), in the temperature region $T \sim v/a$ an important change occurs in the temperature dependence of the fundamental thermodynamic quantities which characterize the intermediate state.

Equations (23) and (25) cease to be valid at temperatures $T \sim v/l$ where l is the mean free path of the electrons. For $T \ll v/l$ a linear temperature dependence for the specific heat should again be observed, and a quadratic dependence for the magnetic moment. The reason for this is that in the region $T \ll v/l$ the principal contribution to the thermodynamic quantities is made by excitations for which l is much less than the length $a/|n_z|$, which must be traversed by the excitation on going from one boundary between phases to the other.

In conclusion, we note that quantization of the energy levels of the electronic excitations can be observed even at temperatures much higher than v/a. For example, let us consider the absorption of high frequency sound in the intermediate state. It is known that the fundamental mechanism of absorption is the decay of sound quanta into "electrons" and "holes," that is, two electronic excitations. Inasmuch as excitations with not too small values of n_z cannot have an energy much smaller than v/a in the presence of quantization, then at the sound frequencies $\omega \ll v/a$ the probability of decay will be much less in comparison with the case of a completely normal metal.

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[1] L. D. Landau, JETP 7, 371 (1937).

[2] A. F. Andreev, JETP 46, 1823 (1964), Soviet Phys. JETP 19, 1228 (1964).

[3] Bardeen, Cooper, and Schrieffer, Phys. Rev. 108, 1175 (1957).

[4] L. D. Landau and E. M. Lifshitz, Élektrodinamika sploshnykh sred (Electrodynamics of Continuous Media) (Fizmatgiz, 1959), pp. 228-236.

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85