The value $\beta=0.470r_s^{1/2}$ is calculated assuming the conduction electrons of the metal to be an electron gas and assuming the possibility of a high-density expansion ($r_s\leq 1$). In real metals r_s is larger than 1, and the high-density expansion should not be correct. However, it is shown that the theoretical value $\beta=0.470r_s^{1/2}$ agrees with the experimental values for various metals, for example, aluminum ($r_s=2.010$) and sodium ($r_s=3.768$). Thus it is concluded that the results gained in this paper should be correct in the range of small r_s. It is desirable to use the experimental data of k_c in the range of large values of r_s. Unfortunately, we have no experimental data on k_c for large values of r_s. But this fact does not prevent us from concluding that positronium formation does not occur in real metals.

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An Additional Equation in the Phenomenology of Superconductivity: Resistive Effects

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We give a phenomenological derivation and a discussion of the "extra Ginzburg-Landau equation" which connects the charge, electrical potential, and time dependence of the order parameter in a superconductor.

Recently Gor'kov[1] pointed out that in his version of the BCS theory of superconductivity the "anomalous" Green's function, $F\sim\langle\psi\psi\rangle$, and thus the energy-gap function Δ and the Ginzburg-Landau order parameter Ψ, vary as $e^{-2i\mu t/\hbar}$, where μ is the Fermi energy. Josephson[2] first noted that this time dependence has observable effects. In particular, it leads to the ac Josephson current in two-superconductor tunnel junctions.

Because of this time dependence, the Fermi level plays a role in the phenomenology of superconductivity different from that in normal metals: it is not only a macroscopic variable determined by local thermodynamic equilibrium, but a microscopic variable determining the local state, which is closely coupled by the long-range order throughout the superconducting circuit.

Corresponding to this duality, we may introduce the chemical potential into the theory in two ways. In both let us first consider an isolated uniform bit of superconductor in equilibrium, later assuming in the standard fashion of nonequilibrium thermodynamics that a steady-state system is made up of many such bits together with the heat and particle flows necessary to maintain quasiequilibrium.

The Hamiltonian of our bit of superconductor is taken as

$$\mathcal{H}=\mathcal{K}+\mathcal{V}_p+\mathcal{H}_{\text{int}}+eVN\,, \tag{1}$$

where $\mathcal{K}$ is the kinetic energy, $\mathcal{V}_p$ is the lattice periodic potential, $\mathcal{H}_{\text{int}}$ is the short-range interaction responsible for superconductivity, V is the mean electrostatic potential including any long-range effect due to a net space charge in the sample, and N is the total electron number. The energy necessary to add a single electron of momentum k in a normal metal with Hamiltonian (1) we define as ϵ_k+eV.

In the standard version of superconductivity theory we add and subtract a term μN, obtaining

$$\mathcal{H}\equiv\mathcal{H}'+\mu N\,. \tag{2}$$

Then the quasiparticle energies and the total many-particle state are calculated for the Hamiltonian $\mathcal{H}'$. The quasiparticle energy is

$$E_k=[(\epsilon_k+eV-\mu)^2+\Delta^2]^{1/2}\,,$$

and has a minimum at the "Fermi surface" where $\epsilon_k+eV=\mu$. The Hamiltonian $\mathcal{H}'$ leads to no time dependence of F and Δ. The number of particles N is not fixed, but the mean value may be obtained in the usual fashion,

$$G(\mu,T)=-kT\ln\text{Tr}\exp(-\beta\mathcal{H}')\,,$$
$$\langle N\rangle=-\partial G/\partial\mu\,. \tag{3}$$

[1] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **34**, 735 (1958) [English transl.: Soviet Phys—JETP **7**, 505 (1958)].
[2] B. D. Josephson, Phys. Letters **1**, 251 (1962).

Reintroducing μN and thus using the *total* Hamiltonian, we find that the only modification necessary is that we must replace

$$\Delta \to \Delta e^{-2i\mu t/\hbar}, \tag{4}$$

or that the Ginzburg-Landau order parameter $\Psi \to \Psi e^{-2i\mu t/\hbar}$, as noted by Gor'kov. Equation (4) is a direct consequence of the Heisenberg equation of motion and the commutator $[N,\Delta]=2$.

Let us now treat the problem in an ostensibly microcanonical fashion. With a *fixed* number of particles N, we shall use only the first three terms of (1) because the last term is constant:

$$\mathcal{H} \equiv \mathcal{H}_0 + eVN. \tag{5}$$

Again we construct

$$F(N,T) = -kT \ln \mathrm{Tr}\, \exp(-\beta\mathcal{H}_0), \tag{6}$$

and the conventional thermodynamic definition of the chemical potential is

$$\mu_c(T,N) = \partial F/\partial N. \tag{7}$$

Basically, μ_c is half the energy necessary to add a pair of electrons to the superconductor, or we could define it as the chemical potential of a normal metal in equilibrium with the superconductor at the same electrostatic potential. Taking account of the electrostatic potential in Eq. (5), equilibrium thermodynamics clearly requires

$$\mu_c + eV = \mu. \tag{8}$$

As we have noted, μ_c is a function of T and N. In the presence of number or thermal variations, we have

$$(\partial\mu_c/\partial N)\delta N + (\partial\mu_c/\partial T)\delta T = \delta(\mu - eV). \tag{9}$$

Equations (8) and (9) are very well known and their development presented here is the standard one, the argument being independent of whether the metal is superconducting or normal. Nevertheless, when combined with Eq. (4), which is characteristic of superconductivity and which is derived easily only in the first scheme, they have consequences which we explore further.

We first observe that in a bulk superconductor with no current flow, for practical purposes N will be fixed and in the presence of a thermal gradient,

$$(\partial\mu_c/\partial T)\nabla T = \nabla\mu - e\nabla V. \tag{10}$$

There will thus be an electrostatic potential gradient in precise analogy to the thermomechanical pressure gradient in liquid helium. Such an effect clearly also occurs in the normal state, but is masked by the usual thermoelectric transport process. Devising an experiment to measure it in the superconducting state also seems difficult.

To learn more about what happens in the presence of a gradient of μ, let us now remove the temperature variation and write

$$(\partial\mu_c/\partial N)e\delta N = e\delta\mu - e^2\delta V.$$

Here we have neglected background space-charge effects, which may be included in a straightforward way. Using Poisson's equation, we may also write this as

$$-(1/4\pi)(\partial\mu_c/\partial\rho)\nabla^2\delta V = e\delta\mu - e^2\delta V,$$

where ρ is the number density, or

$$-\lambda_D{}^2\nabla^2\delta V = (\delta\mu/e) - \delta V.$$

This equation defines the Debye screening length λ_D. It is instructive to rearrange the right-hand side by using the identity

$$\mu = \frac{i\hbar}{4|\Psi|^2}\left(\Psi^*\frac{\partial\Psi}{\partial t} - \frac{\partial\Psi^*}{\partial t}\Psi\right),$$

which follows from Eq. (4). Introducing the superfluid fraction $n_s \equiv |\Psi|^2$, and the normal fraction $n_n = 1 - n_s$, we find

$$\lambda_D{}^2\nabla^2\delta V = (1/e)\left[\tfrac{1}{4}\Psi^*(i\hbar(\partial/\partial t) - 2e\delta V)\Psi + \mathrm{c.c.} + n_n(\delta\mu - e\delta V)\right]. \tag{11}$$

This is the "extra Ginzburg-Landau equation" which has been proposed elsewhere by one of the authors.[3] Essentially identical, or closely similar, equations have been derived directly from Green's function theory by Stephen and Suhl[4] and by one of us.[5] It is for that reason that we have made the rather artificial transformations which lead to Eq. (11) from the simpler and more physical Eqs. (4) and (9).

It is interesting to note the formal similarity between the terms of Eq. (11) (excluding the last one in n_n) and those of the Ginzburg-Landau current equation. That is, (11) is an equation for the charge fluctuation containing a time derivative and the scalar potential, and thus is formally a fourth, "time-like" component of the GL current equation,

$$\lambda_L{}^2\nabla^2\mathbf{A} = \frac{c}{4e}\left[\Psi^*\left(i\hbar\nabla + \frac{2e}{c}\mathbf{A}\right)\Psi + \mathrm{c.c.}\right]. \tag{12}$$

The two are not equivalent, however: λ_D, the Debye length, enters into the longitudinal Eq. (11), while λ_L, the London length, determines the current in Eq. (12). The fact that the ratio $c\lambda_D/\lambda_L = v_F/\sqrt{3}$ is the velocity of collective excitations in the superconductor is closely related to the preservation of gauge invariance, as discussed by Ambegaokar and Kadanoff.[6] Also, of course, Eq. (11) has a response contribution from the normal fraction, and it could in principle also contain the thermal terms.

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Since in fact λ_D is very small, the left-hand side of Eq. (11) is negligible in the absence of thermal gradients. We then see that a potential gradient, and hence a resistance, is possible in a superconductor, but only in association with a time dependence of Ψ. Such a time dependence can occur by acceleration of a current, but seldom will; quite commonly, however, it is effected by the flow of magnetic vortex lines through a sample, since the passage of one vortex between two points requires a change of 2π in the relative phase of Ψ at those points.

Finally, we note that our basic equations are (4) and (9) and that the GL charge equation (11) follows from them. Furthermore, the derivation of (9) must be regarded as phenomenological because of the focus of attention on a "small" bit of superconductor in equilibrium. The present arguments do not include a specification of a minimum size for such a bit, and hence do not give a scale of lengths over which Eqs. (9) and (11) can be expected to hold. In fact, the more fundamental Green's function derivation of Eqs. (11) and (12) contains the requirement that disturbances be slowly varying in both space and time.

It is also worth noting that the GL equation (12) together with Eq. (4) may be used for a very compact derivation of a previously known result concerning the thermopower of a superconductor.[7] If the phase of the order parameter is $-2\mu t$, then the time derivative of the supercurrent is

$$\partial j/\partial t = (\rho_s e/m)(-\nabla\mu + eE). \quad (13)$$

Equation (13) shows that the emf in a closed circuit must be zero under conditions of zero current, and hence proves that a superconductor has zero thermopower.

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Low-Field de Haas–van Alphen Effect in Ag

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Detailed studies of the de Haas–van Alphen (dHvA) effect in Ag single crystals have been carried out with a high-sensitivity torque magnetometer in steady fields up to 40 kG. The angular variations of all of the pertinent dHvA frequencies were determined to better than 0.1%. We were able to achieve this precision by observing oscillations in the torque as the magnetic field was rotated with respect to the samples at a fixed magnetic field. More data have been obtained on the new low-frequency oscillations which we recently reported, and evidence is presented which suggests that these oscillations may be associated with a difference frequency between two extremal belly orbits.

INTRODUCTION

The detailed study of the de Haas–van Alphen (dHvA) effect in Ag by Schoenberg[1] showed that the Fermi surface (FS), like that in Cu, could be represented by a single sheet which is multiply connected along the ⟨111⟩ directions. These measurements provided sufficient information about the FS to allow a mathematical description[2] of the shape of the surface, although several features of the surface could not be investigated in detail by pulsed-magnetic-field techniques. In an attempt to complete the experimental picture we have undertaken a systematic study of the dHvA effect in Ag by means of the steady-field torsion-balance method. In the initial phase of this study a new low-frequency oscillation F_c was observed[3] which appeared to be inexplicable in terms of the above model of the FS, and was therefore tentatively attributed to a small pocket of electrons in the second Brillouin zone, centered at the symmetry point L. Further studies of these oscillations have cast some doubt on this interpretation and have led to an alternative explanation based on a nonlinear oscillatory effect of the type first considered by Shoenberg.[1,4] In effect, electrons in the metal experience a field $B=H_0+4\pi M$ rather than the applied field H_0. When M, and hence B, is oscillatory, Shoenberg has shown that the dHvA oscillations have an unusually large harmonic content. He also pointed out that if more than one dHvA frequency is present, sum and difference frequencies may be generated. Accordingly, the low frequency F_c may arise as a difference frequency between two dHvA oscillations rather than from a new segment of the FS. The origin of F_c can thus be traced to the existence of *two* extremal belly orbits, whose

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