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## ON THE SUPERCONDUCTIVITY OF ELECTRONS AT THE SURFACE LEVELS

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AS far back as 1932<sup>[1]</sup>, I. E. Tamm pointed out the possibility of the existence of surface levels, i.e., electron states localized on the crystal surface. The problem of surface levels has subsequently been dealt with many times (see, for example, <sup>[2]</sup>) but their influence on the properties of a crystal have until now remained, to the best of our knowledge, insufficiently clear. On the one hand, this is due to the nonideal state of the real crystal surface, the presence of adsorbed layers, etc. On the other hand, even if the surface were ideal, it would be difficult to observe the additional conduction due to the presence of partly filled surface levels because of the shunting action of the volume conduction.

The surface conduction would play an important role if the surface electrons (the electrons at the surface levels) were able to go over into the superconducting state. And in this connection, the question arises whether the Cooper effect<sup>[3]</sup> is possible in the case of surface electrons.

It is easy to show that in a two-dimensional system even the smallest resultant attraction between the particles should give rise to the formation of correlated pairs and the appearance of a gap in the spectrum of one-particle excitations. Using the interaction Hamiltonian<sup>1)</sup>

$$H' = \frac{\lambda}{2} \int d^2x (\bar{\psi} (\bar{\psi}\psi) \psi), \quad \lambda < 0, \quad (1)$$

we can easily prove that the usual discussion (see, for example, <sup>[4]</sup>) remains completely valid if the two-dimensional quantities are everywhere replaced by three-dimensional ones. In particular, the excitation spectrum is given by the expression  $\epsilon_p = [v^2(p-p_0)^2 + \Delta^2]^{1/2}$ , where  $v$  is the velocity on the Fermi boundary and  $p_0$  is the momentum at the boundary, related to the electron density  $\rho$  by the expression  $\rho = p_0^2/2\pi$ . The equation for the determination of the gap  $\Delta$  at  $T = 0$  has the form

$$1 = - \frac{\lambda}{2(2\pi)^2} \int \frac{d^2p}{\epsilon_p}. \quad (2)$$

Integrating Eq. (2) with respect to  $x = v(p-p_0)$  between the limits  $-\omega_D$  and  $\omega_D$ , where  $\omega_D \ll vp_0$ , we obtain

$$\Delta = 2\omega_D \exp(-2\pi/m|\lambda|). \quad (3)$$

On the other hand, in the three-dimensional case, the well-known Bardeen, Cooper, and Schrieffer expression (see <sup>[4]</sup>) has the form  $\Delta' = 2\omega_D \times \exp(-2\pi^2/mp_0|\lambda'|)$ , where  $\lambda' \equiv V$  is a three-dimensional interaction constant of the type given by Eq. (1) and  $N(0) = mp_0/2\pi^2$  is the density of states at the Fermi boundary.

The sign of the interaction constant  $\lambda$ , as in the volume problem, cannot be found reliably. Therefore, we shall restrict ourselves to indicating the existence of the effects (among them is the exchange between surface phonons corresponding to Rayleigh waves) which probably make a contribution to the attraction between electrons additional to that which obtains in the interior. In any case, we cannot exclude the possibility that under certain conditions the sign of  $\lambda$  may be negative. If the interaction between electrons (one-particle excitations) in the three-dimensional and two-dimensional cases is of the same order, then  $\lambda \sim p_0\lambda' \sim \lambda'/a$  and  $\ln \Delta \sim \ln \Delta'$  (here  $a \sim 3 \times 10^{-8}$  is the lattice constant and it is assumed that  $\hbar = 1$  everywhere).

When  $\lambda < 0$ , the surface electrons go over into the superconducting state. At the same time, in the interior of the metal, there may be no attraction or at least it may be represented by a different value of the gap. In the latter case, the surface superconductivity should be noticeable only when the gap (and that means also the critical temperature) is smaller for the volume superconductivity than for the surface superconductivity. We note that, in addition to the surface superconductivity of this type in metals, we can have in principle another case when the electrons at the levels of the volume type experience excess attraction only near the surface. However, we shall

not discuss further this effect, which is the special case of surface ordering.<sup>[5]</sup>

The possibility of the existence of surface superconductivity in dielectrics is very interesting. If the surface levels at  $T = 0$  are not filled under normal conditions,<sup>[6]</sup> they can be partly filled by charging the surface; under favorable conditions, the attainable surface-charge density  $\sigma \sim en \sim 10^4$  may be sufficient for this purpose (here  $n \sim 10^{14}$  is the number of filled surface levels per unit area). In general, the number of surface levels per unit area is of the order of the number of atoms, i.e.,  $n \sim a^{-2} \sim 10^{15}$ . Therefore, in the majority of cases, it is not possible to fill artificially the surface band.

The influence of a magnetic field and of a current on the surface superconductivity can be understood qualitatively by assuming that we are dealing with the usual superconducting film whose thickness is, however,  $l \sim a \sim 3 \times 10^{-8} \sim 10^{-7}$  cm. The critical field in the film<sup>[7]</sup> is  $H_C = (\sqrt{24} \delta_0 / l) H_{Cm} \sim 10^3 H_{Cm} \sim 10^{-5}$  Oe, if the "volume" values  $\delta_0 \sim 10^{-5}$  cm and  $H_{Cm} \sim 10^2$  Oe are used for the surface superconductivity.<sup>2)</sup> In the cylindrical geometry case<sup>[7]</sup>,  $H_C H_{Ic} = \frac{8}{3} H_{Cm}^2$ , where  $H_{Ic}$  is the field on the surface of a cylinder with radius  $r$  for a critical current  $I_c = \frac{1}{2} cr H_{Ic}$ . Under these conditions  $H_{Ic} \sim 10^{-3} H_{Cm} \sim 0.1$  Oe.

<sup>1)</sup>Here and later we assume, as usual, that the region of interaction is of width  $2\omega_D$  near the Fermi boundary ( $\omega_D$  is the Debye frequency). The field operators in Eq. (1) are two-dimensional and the symbol  $d^2$  represents a two-dimensional differential.

<sup>2)</sup>The film is assumed to be an open surface (we are considering a superconducting region of the crystal surface between two contacts). If the film is closed, its behavior in an external field is more complex (see<sup>[8]</sup>).

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## INVESTIGATION OF THE MAGNETIC PROPERTIES OF DIBENZENECHROMIUM AND DITOLUENECHROMIUM IODIDES AT VERY LOW TEMPERATURES

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IN an earlier work<sup>[1]</sup>, the present authors and Chibrikov investigated the hyperfine interaction of an unpaired electron with the protons in the molecules of paramagnetic cations of dibenzenechromium (DBC) and ditoluenechromium (DTC) and measured their magnetic susceptibility in the temperature range from 1.3 to 295°K. It was found that the unpaired electron in these compounds was localized mainly at the chromium atom and that the magnetic susceptibility of these compounds in the cited temperature range obeyed the Curie-Weiss law  $\chi = C/(T - \Theta)$ , where  $\Theta_{DBC} = -4.6 \pm 0.2$  deg K and  $\Theta_{DTC} = -2.0 \pm 0.2$  deg K, and the value of the constant  $C$  represents one electron spin per molecule.

It was of interest to extend these measurements to very low temperatures. For this purpose, we constructed a device which made it possible to investigate the proton resonance in the temperature range from 0.1 to 1.5°K. Very low temperatures were obtained by adiabatic demagnetization of iron-ammonium alum. The investigated powder sample was in a small glass ampoule; a copper cold duct entered the ampoule and its other end was pressed in the usual way into a pellet of the paramagnetic salt. Thermal contact between the sample and the cold duct was ensured by filling the ampoule containing the sample with carbon tetrachloride.

The pellet and the sample were in an hermetically sealed glass jacket, into which a small amount of helium was admitted at room temperature; at very low temperatures, the helium was sorbed by the alum, which ensured thermal insulation between the sample assembly and the helium bath. The coil of a Pound-type oscillator, used to measure the resonance, was wound on the outside of the glass jacket. The temperature was determined from the susceptibility of the paramagnetic salt. A control experiment showed that the sample temperature did not differ, within the experimental error ( $\pm 5\%$ ), from the temperature