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Letters to the Editor

POSSIBILITY OF THE OCCURRENCE OF SUPERCONDUCTIVITY IN THIN NON-METALLIC FILMS

B. A. TAVGER and V. Ya. DEMIKHOVSKIĬ

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THE phenomenon of superconductivity in thin films has its own specific peculiar features. A large number of papers is devoted to this problem [1]. In these papers metallic films are considered in which the quantization of the transverse motion of the electron is not essential. However, in considering semiconducting, semimetallic and dielectric thin films it is necessary to take such quantization into account. The present paper is devoted to this problem.

In a film the transverse component of the quasimomentum k_z is not defined. Therefore, the state and the energy of the electron are determined by the longitudinal components of the quasimomenta k_x, k_y and the discrete quantum number n. As a result quasidiscrete levels $\epsilon(k_x, k_y, n)$ appear—the sub-bands. The case when only one sub-band ($n = 1$) is occupied is of interest. In this case the occupied electron states lie in one cross section of a Brillouin zone. And although a crystalline film is a three-dimensional structure in coordinate space (the thickness of the film $2l$ remains much larger than the lattice constant a), the momentum space becomes two-dimensional. The reduction indicated above of a three dimensional Brillouin zone to a two dimensional one can lead to certain peculiar features in superconductivity. The conditions which lead to the occupation of only one cross section of a Brillouin zone were investigated by us previously.[2] Comparatively low temperatures ($\kappa T \ll \epsilon(2) - \epsilon(1)$, where κ is the Boltzmann constant) and low carrier concentrations are required.

The temperature condition for superconducting films is well satisfied for thicknesses smaller than 10^{-5} cm. Indeed, the electron energy can be evaluated in the effective mass approximation, if we consider also that n defines the quantized value of k_z. We have $\epsilon \sim (\hbar^2/2m^*)(\pi/l)^2n^2$. For thicknesses of $2l \sim 10^{-5}$ cm we obtain $\epsilon(2) - \epsilon(1) \sim 10°$K. The condition limiting the carrier concentration already from considerations of dimensionality must have the form

$$N < A/(2l)^3, \qquad (1)$$

where A is a dimensionless factor which depends on the specific dispersion law. According to the estimate carried out in reference [2] in the case of an isotropic quadratic dispersion law A is of the order 10. Condition (1) can be realized in semiconducting, semimetallic, and dielectric films. Below we assume that condition (1) is satisfied; thereby we exclude metallic films from consideration.

As is well known, superconductivity is determined by the electron-phonon interaction. Phonons in thin films also have specific characteristic features in virtue of definite boundary conditions. However, if the film lies on a substrate, and the two have similar elastic constants, the phonon system in the film and in the substrate differs little from phonons in a bulk sample. Superconductivity depends essentially on the interaction of electrons with short wavelength phonons of wavelength $\lambda \ll 2l$. Therefore, in a free film the phonon spectrum can also be assumed to be the same as in a bulk sample. It is true that an additional) contribution to the electron-phonon interaction will also be made by the surface (Rayleigh) waves. But since the present note does not claim to give an exact quantitative investigation we choose for the subsequent discussion the following simplified model: the electron states lie in one plane cross section of a Brillouin zone, while the phonon spectrum is the same as in a bulk sample.

When condition (1) is satisfied the component of the quasimomentum of electrons k_z is not defined and has a spread $\Delta k_z \sim \pi/l$. Therefore, the electron-phonon interaction will essentially involve phonons with a transverse component of the quasimomentum in the range from $-\pi/l$ to π/l, i.e., only those phonons will be essential for the interaction which lie in one layer of a Brillouin zone. Thus, when condition (1) is satisfied the problem of the electron-phonon interaction in thin films reduces to a plane problem similarly to the case investigated in reference [3].

The usual procedure for finding the energy gap at a temperature of absolute zero (cf., for example, [4,5]) leads in our case to an equation similar to the equation for a bulk superconductor:

$$1 = \frac{g}{2V}\sum_{k'} (\Delta^2 + \xi_{k'}^2)^{-1/2}, \qquad \xi_k = \frac{\hbar^2 k^2}{2m^*} - \mu, \qquad (2)$$

where V is the volume of the film. A distinctive feature of Eq. (2) is the summation with respect to k over a two-dimensional Brillouin zone. The interaction constant g, generally speaking, differs somewhat from its value in a bulk sample. However, this does not involve a difference in principle, since g is determined by the phonon energy, and the energy spectrum here is the same as in a bulk sample.

The problem of the electron-electron interaction is in our case, of course, also a plane problem. Therefore, just as in the three-dimensional case [5] the Coulomb repulsion can be taken into account by including it in the constant g.

By going over in (2) from summation to integration and assuming, as usual, $\hbar\omega_c \ll \mu$, we obtain

$$\Delta = 2\hbar\omega_c \exp\left(-\frac{2\pi}{g}\frac{2l\hbar^2}{m^*}\right). \qquad (3)$$

However, in our discussion condition $\hbar\omega_c \ll \mu$ need not be satisfied. In the opposite case when $\hbar\omega_c \gg \mu$ the index in the exponential can be larger by a factor of two. In the general case this index will have an intermediate value. Similarly we can show that the relation between the critical temperature and the energy gap will at T = 0 be the same as for bulk samples, i.e., $2\Delta = 3.52\kappa T_c$.

Formula (3) can be written in another form:

$$\Delta = 2\hbar\omega_c \exp\left(-1 / gN_{\mathrm{film}}\right), \qquad (4)$$

where

$$N_{\mathrm{film}} = \frac{1}{2\pi}\frac{1}{2l}\frac{m^*}{\hbar^2} = N_{\mathrm{bulk}}\frac{\pi}{k_F \cdot 2l} \qquad (5)$$

is the density of electron states per cm^3 of the film. The form of expression (4) agrees with the form of the expression for the gap in a bulk sample, but the density of electron states will be different. It can be seen from (5) that the magnitude of the gap does not depend on the energy and, consequently, on the carrier concentration (when condition (1) is satisfied). Another characteristic feature is the dependence of the gap on the thickness of the film: as the film thickness diminishes the gap grows exponentially. As l approaches cell dimensions the density of states in a film of any material becomes in order of magnitude equal to the maximum possible density (i.e., to the density of states in a metal).

Schooley et al.[6] have stated that the semiconductor $SrTiO_3$ becomes a superconductor at concentrations greater than 7×10^{17} cm^{-3}. From (5) it can be easily seen that the density of states corresponding to the indicated concentration in a bulk sample can be obtained for a film thickness $2l \sim 0.5 \times 10^{-6}$ cm independently of the carrier concentration, in particular also at lower concentrations.

From the results obtained above one can draw the conclusion that substances with g > 0 can become superconductors even at very low concentrations of carriers, if they are prepared in the form of a sufficiently thin film. In other words, if a substance has due to a very low concentration of carriers a very low critical temperature which is not observable experimentally, then by preparing it in the form of a thin film one can raise the critical temperature up to observable values.

In real polycrystalline films due to the scattering of electrons at grain boundaries the longitudinal components of the quasimomentum k_x and k_y are not good quantum numbers, as was assumed above. However, just as in the three-dimensional case [7], it can be shown that this circumstance does not essentially alter the parameters of superconductivity as long as the mean free path, which is of the order of the grain size, is much larger than a.

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