On the efficiency of the exciton mechanism of superconductivity in films

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The effect of excitonic excitations localized in a semiconducting coating on the critical temperature of superconducting films is considered (see also [4-6]). Numerical estimates are given for the contribution of such excitations to the electron pairing interaction constant for coatings with various forms of the dielectric permittivity $\epsilon(\omega,q)$.

A large and ever-increasing number of investigations are being devoted at the present time to a search for materials with high temperatures of the superconducting transition T_c. Preliminary estimates (see, for example,[1]) show that a great deal can be expected from materials and systems in which the so-called "excitonic" mechanism of superconductivity is realized. Special interest is attached here to layered systems of the sandwich type. In particular, the problem of the effect of a dielectric coating on the superconducting properties of films has been studied previously.[2,3]

Inasmuch as a different variant of such a system has been studied by Allender, Bray and Bardeen,[4] who considered a very thin metallic film evaporated onto a semiconductor, for example, Ge or InSb. The excitonic mechanism in the given case consists in the fact that electrons tunneling into the semiconductor from the metallic film will, in addition to the usual exchange of phonons, also exchange electronic excitations, producing a hole in the valence band of the semiconductor and an electron in the conduction band. According to estimates of the authors, this should lead to a significant increase in T_c, and the fundamental contribution to the superconductivity will be made by the region of frequencies where the imaginary part of the dielectric permittivity $\operatorname{Im}\epsilon_S(\omega, q)$ has a peak which, for semiconductors, corresponds to the region of interband transitions.

Meanwhile, it is known that the frequencies of the elementary excitations correspond to the zeros of $\epsilon(\omega, q)$ and, correspondingly, the fundamental contribution to the formation of Cooper pairs is made by the frequency regions containing peaks not of $\operatorname{Im}\epsilon(\omega, q)$ but of $\operatorname{Im}[1/\epsilon(\omega, q)]$[5]. The latter circumstance is very important, since the peak of $\operatorname{Im}[1/\epsilon(\omega, q)]$ is very weak in the region of interband transitions, and for some semiconductors almost nonexistent.

As pointed out by Inkson and Anderson,[6] the screening factor was taken into account twice in the work of Allender, Bray and Bardeen in the calculation of the electron-electron interaction induced by exchange of excitons. It seems to us, however, that it is more significant that, for further estimates, this screening factor of Allender, Bray and Bardeen is replaced by a numerical coefficient, the frequency dependence of the screening is ignored, and an expression is used for $1/\epsilon(\omega, q)$ that is actually obtained in second-order perturbation theory:

$$\frac{1}{\varepsilon(\omega,q)}=1-\frac{4\pi e^2}{q^2}\Pi_0(\omega,q),$$

where $\Pi_0(\omega, q)$ is the usual polarization loop for electrons in a semiconductor. At the same time, Allender, Bray and Bardeen apply the exact rule of sums

$$\int_0^\infty \varepsilon_2(\omega)\,d\omega=\frac{4\pi e^2}{q^2}\int_0^\infty \operatorname{Im}\Pi(\omega,q)\,d\omega,$$

using the random phase approximation for ϵ[7], when

$$\varepsilon(\omega,q)=1+\frac{4\pi e^2}{q^2}\Pi_0(\omega,q).$$

This implicit joint use of two different approximations for $\epsilon(\omega, q)$ is, in our opinion, the basic reason for the divergence of Allender, Bray and Bardeen's analysis from the generally accepted point of view.[5,6]

We now try to estimate directly the possible effect on T_c of a metallic film of electronic excitations in a semiconductor coating. We begin from the following general expression for the coupling constant, which characterizes the interaction of the electrons with the elementary excitations:

$$\lambda=-\frac{2}{\pi}\frac{1}{v_F^2}\sum_{kk'}\int\frac{d\omega}{\omega}\operatorname{Im}V_{kk'}(\omega)\Big/\sum_{k'}\frac{1}{v_F};\qquad(1)$$

$$V_{kk'}(\omega)=\int\int dr dr'\psi_k^*(r)\psi_{-k}^*(r')V(r,r',\omega)\psi_{k'}(r')\psi_{-k'}(r'),\qquad(2)$$

$$V(r,r',\tau)=\frac{1}{2\pi}\int_{-\infty}^{\infty}V(r,r',\omega)e^{i\omega\tau}d\omega.$$

Here $V(r, r', \tau)$ is the delayed interaction of two electrons located at the points r and r'; $\psi_k(r)$ are the electronic wave functions, and summation is carried out over the states lying on the Fermi surface. It is easy to see that if we integrate only over the phonon frequency range in (1), then we obtain the usual expression for the electron-phonon coupling constant.[8] The coupling constants of the other excitations are expressed in Eq. (1) if integration in ω is taken over the range of frequencies characteristic for these excitations.

The interaction $V(r, r', \omega)$ can be a very complicated function, to which the various elementary excitations (including those localized only near the boundary of the film, see, e.g.,[9]) make a contribution. Let us estimate the contribution to the interaction of the electron excitations localized in the semiconductor coating. Here we shall assume the electronic functions $\psi_k(r)$ to be plane waves which have a nonvanishing amplitude in the metallic film and in a thin layer of the coating with thickness on the order of the penetration depth of the conduction electrons in the semiconductor. Then we obtain in the simplest approximation for the interaction energy

$$V_{kk'}(\omega)=\frac{\alpha}{V}\frac{4\pi e^2}{q^2}\frac{1}{\varepsilon(\omega,q)},\qquad(2')$$

where $q = |k = k'|$ and $\epsilon(\omega, q) = \epsilon_S(\omega, q) + k_D'^2/q^2$. Here $\epsilon_S(\omega, q)$ is the dielectric permittivity of the bulky semiconductor and the term $k_D'^2/q^2$ takes into account the screening of the interaction by conduction electrons which tunnel from the metallic film into the semiconductor. The numerical coefficient α appears in (2) because the electrons conduct only part of the time in the semiconductor coating[4]. The value of this coefficient

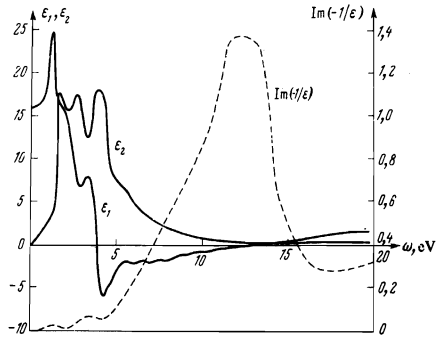

FIG. 1.

is determined by the thickness of the metallic film and by the height of the potential barrier on the metal-semiconductor boundary.

Unfortunately, the dielectric permittivity $\epsilon_S(\omega, q)$ has a complicated form and is known only for a few semiconductors. Therefore, we limit ourselves to the simple interpolation formula:

$$\varepsilon_s(\omega, q)=1+\left(\frac{1}{\varepsilon_s(\omega,0)-1}+\frac{q^2}{k_D^2}\right)^{-1}, \tag{3}$$

where k_D is the reciprocal of the screening radius, which depends on the density of the valence electrons in the semiconductor. A comparison of the $\epsilon_S(\omega, q)$ obtained from Eq. (3) with the pseudopotential calculations of Walter and Cohen for Si[10] shows that excellent quantitative agreement is observed for the case $q/k_D \leq 0.14$ but for $q/k_D = 0.56$, although it correctly conveys the basic qualitative features of the behavior of $\epsilon_S(\omega, q)$, the formula understates the value of $\mathrm{Im}[1/\epsilon_S(\omega, q)]$ by a factor of about two (we shall see below that this fact turns out to be unimportant for the estimates given below).

We now estimate the contribution to superconductivity from the frequency range of the interband transitions, i.e., the range in which the value of $\mathrm{Im}\,\epsilon_S(\omega, q)$ is maximal in semiconductors. According to Allender, Bray and Bardeen, it is precisely this range of frequencies which can make for a large coupling constant and lead to a significant increase in the T_c of the film. With account of the approximations mentioned above, we have

$$\begin{aligned}\lambda_{ex}&=-\frac{2}{\pi}\frac{\alpha}{Vv_F}\sum_q\frac{4\pi e^2}{q^2}\int\frac{d\omega}{\omega}\mathrm{Im}\frac{1}{\varepsilon(\omega,q)}\\&=-\frac{2\alpha}{\pi v_F}\frac{2S_F}{(2\pi)^3}\frac{4\pi e^2}{\bar q^2}\int\frac{d\omega}{\omega}\mathrm{Im}\frac{1}{\varepsilon(\omega,\bar q)},\end{aligned} \tag{4}$$

where $\bar q$ is some mean value of the transferred momentum, S_F is the area of the Fermi surface, and integration is carried out over the region of frequencies of the interband transitions.

In order to obtain a numerical estimate of λ_{ex}, we shall assume the film to be niobium and the coating to be of such a typical semiconductor as InSb. Figure 1 shows the frequency dependence $\epsilon_S(\omega, 0) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ and the function $\mathrm{Im}[1/\epsilon_S(\omega, 0)]$ for InSb, taken from the work of Philipp and Ehrenreich,[11] which we used in carrying out the numerical calculations, and Fig. 2 gives the dependence $f(\omega) = \omega^{-1}\,\mathrm{Im}\,\epsilon^{-1}(\omega, \bar q)$ obtained for values of the parameters $\bar q/k_D = 0.63$ and $k_D'/k_D = 0.45$. As is seen from Fig. 2, the value of $f(\omega)$ does not have a sharply expressed interband peak, although in the intervals 0.5 eV < ω < 3.0 eV and 3.0 eV < ω < 7.5 eV there are nevertheless small peaks

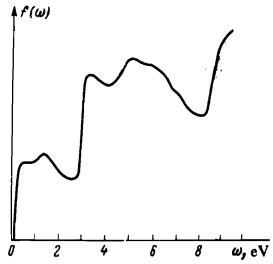

FIG. 2.

with coupling constants of $\lambda_{ex}^{(1)} = 0.04\,\alpha$ and $\lambda_{ex}^{(2)} = 0.14\,\alpha$, respectively. If we take the most favorable variant, when the metallic film borders on the semiconductor on two sides, and assume the thickness δ of the effective layer of penetration of electrons into the semiconductor to be equal to 2.5 Å and the thickness of the film to be L = 10 Å, then $\alpha = 2\delta/(2\delta + L) = 0.33$. Even if we take into account that Eq. (4), may give too small a result by a factor of two because of the inaccuracy of Eq. (3), λ_{ex} still turns out to be too small to increase significantly the transition temperature of the metallic film.

The obtained result follows from the features of the behavior of $\epsilon_S(\omega, q)$ in the range of interband transitions and is not difficult to understand. Actually, it is known from optical measurements (see, for example, Fig. 1) that the dielectric permittivity of the semiconductor has a number of closely spaced strong resonances in the range of interband transitions, and this leads to a large value of the imaginary part of $\epsilon_S(\omega, 0)$ over this entire range. As a consequence, the quantity

$$\mathrm{Im}\frac{-1}{\varepsilon_s(\omega,0)}=\frac{\varepsilon_{2s}(\omega,0)}{\varepsilon_{1s}^2(\omega,0)+\varepsilon_{2s}^2(\omega,0)}\leqslant\frac{1}{\varepsilon_{2s}(\omega,0)}$$

turns out to be small, and this predetermines the small effect of the interband transitions on the superconducting properties of the system (see also[6]).

What has been stated above applies to materials with dielectric permittivity of the type shown in Fig. 1. We now estimate by how much the T_c of the film can be increased by the successful choice of a coating material, when $\mathrm{Im}[-1/\epsilon_S(\omega, 0)]$ has a strong peak at a frequency of the order of 0.5–1.0 eV. As an example, we consider the case in which the coating material has a single strong resonance $\epsilon_S(\omega, 0)$, i.e., we shall assume that

$$\varepsilon_s(\omega,0)=\varepsilon_\infty+f/(\omega_1^2-\omega^2-i\delta),$$

where $f/\epsilon_\infty\omega_1^2 \gg 1$, and $\epsilon_\infty > 1$ because of other resonances with much greater frequencies. (Such resonance behavior of $\epsilon_S(\omega, 0)$, in association with electron excitations is observed, for example, in some dyestuffs, and also in aromatic compounds of the anthracene type). It is easy to see that $\omega^{-1}\,\mathrm{Im}[1/\epsilon_S(\omega, 0)]$ has a strong peak at a frequency $\omega_{ex}^2(q = 0) = \omega_1^2 + f/\epsilon_\infty \gg \omega_1^2$, which corresponds to a zero of $\epsilon_S(\omega, 0)$. The range of frequencies near this peak, if we use the same approximations as in the estimate of the role of interband transitions, gives the following contribution to the coupling constant:

$$\lambda_{ex}=\frac{\lambda_0\alpha}{\bar q^2}\frac{k_D^2}{\varepsilon_\infty-1+\gamma}\frac{k_D^2}{(k_D^2+k_D'^2+\bar q^2)^2}\frac{f}{f+\omega_1^2(\varepsilon_\infty-1+\gamma)},$$

$$\gamma=\frac{k_D^2(k_D'^2+\bar q^2)}{\bar q^2(k_D^2+k_D'^2+\bar q^2)},\quad \lambda_0=\frac{S_Fe^2}{\pi^2v_F\hbar^2k_D^2}.$$

In order to estimate the quantity λ_{ex} numerically, we shall, as before, assume the metallic plate to be of niobium and use the same values of the parameters:

$\bar{q}/k_D = 0.63$, $k_D'/k_D = 0.45$, and $\alpha = 0.33$. If we set $f/\omega_1^2 = 20$ and $\epsilon_\infty = 3$, then we find $\lambda_{ex} = 0.47$ and, estimating the transition temperature from the interpolation formula of Allendar, Bray and Bardeen and taking $\omega_c = 10$ eV, $\omega_{ex} = 1.0$ eV, and $\mu = 1/3$, we obtain the relatively high value $T_c = 45°K$.

It must be noted that the excitonic mechanism of superconductivity in films exists only in a thin layer of coating, the thickness of which is of the order of the penetration depth of the conduction electrons. If the excitonic mechanism worked through the entire volume of the sample, then it would be possible to expect a much larger value of T_c. But even in films, given a successful choice of the parameters of the system, when the material of the coating has a strong peak in $\mathrm{Im}\,[1/\epsilon_S(\omega, 0)]$, the film is sufficiently thin, and the potential barrier between the film and the coating is low, the increase in T_c can turn out to be significant.

In this setting, prospective materials for the coating include molecular crystals, which have rather large oscillator strengths in the range of exciton frequencies (especially if we were to succeed in this case in achieving a great penetration depth for the conduction electrons). Therefore, there appear to us to be insufficient grounds for the skepticism as to the possibility of the realization of the excitonic mechanism in films that has been expressed in certain papers.[6,12]

In conclusion, we take this occasion to thank V. L. Ginzburg for discussions and useful comments.

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