

V. M. Agranovich, Yu. E. Lozovik and A. G. Mal'shukov. Electronic Restructuring at the Dielectric-Metal Boundary and the Search for High-Temperature Superconductivity. There are many examples of concrete physical situations whose analysis requires knowledge of the spectrum of excited states of the interface between two media. Such situations arise not only in physics, but also, for example, in physical chemistry (in analysis of the catalytic action of the surfaces of solids), in biophysics, etc.

The present paper concentrates its attention on features of the excited-state spectrum of the metal-dielectric contact, which are important, for example, in connection with the search now being conducted for high-temperature superconductors with the exciton mechanism of electron pairing in the sandwich model^[1]. Since the region of interaction with the dielectric extends only to a distance on the order of a few lattice constants, even under the conditions of ideal contact for conduction electrons on the Fermi surface in a thin metal film (10–30 Å), excited states of the contact layer of the dielectric are found to be highly important. At the same time, it is these excited states that are most strongly influenced by the conduction electrons of the metal. Under these conditions, the aforementioned problem of the exciton electron-pairing mechanism reduces substantially to the problem to be discussed below: that of electron and exciton restructuring in the region of the contact (estimates of the role of the exciton mechanism of superconductivity were given in the reviews^[1,2] and in^[3,4] without consideration of restructurings of this type).

Let us first consider the excitation spectrum of a molecular crystal bordering on a metal^[5]. It is clear even from qualitative considerations that not only Frenkel' volume excitons, but also new exciton states may appear localized near the boundary of the molecular crystal in such a system. In fact, a dipole P situated at a distance z from the boundary is attracted to the polarization that it induces in the metal, and the corresponding potential energy of the electrostatic image of the dipole is $u(z) = -\alpha P^2 (2z)^{-3}$ where $\alpha \sim 1$ is a constant that depends on the orientation of the dipole. If, therefore, there is a depole vibration with frequency ω_f in a molecule at a distance z from the metal and $\omega_f \ll \omega_p$, the plasma frequency of the metal (the quasistatic approximation is justified), then the presence of the image forces results in a shift of the vibration frequency, with $\Delta\omega \approx -A/(2z)^3$, $A > 0$. In quantum language, this means that the Frenkel' excitons corresponding to $0 \rightarrow f$ transitions move in a potential well near the boundary with the metal. Surface excitons (SE) localized near the boundary by electrostatic image forces correspond to the bound states in this well. An actual calculation of the surface-exciton spectrum^[5] takes account of the interaction of the ex-

cited molecule not only with the polarization of the metal that it itself induces (the "self-image"), but also with the polarization induced by other molecules. Also taken into account is the difference in the image potential $u(z)$ at very small distances from the boundary that results from consideration of the penetration of the molecular field into the metal and of the dynamic response lag of the metal's electrons. It is found that not only macroscopic SE, but also states that localize only in the planes of the crystal nearest to the metal may appear for SE in the electronic region of the spectrum. The spectrum of these SE cannot be obtained within the framework of a macroscopic description; it must be calculated for a concrete microscopic model. It is, however, clear that precisely these strongly localized SE may be of particular importance for the exciton mechanism of superconductivity.

Let us now discuss the change in the electron spectrum of a semiconductor under the influence of a metal substrate^[6]. At distances of more than a few angstroms from the boundary, it can be assumed that the interaction of quasiparticles of the semiconductor with the polarization of the metal that they induce can also be taken into account electrostatically, with the aid of image potentials. Thus, the potential energy $V = -e^2/\epsilon\rho$ (of two quasiparticles or quasiparticles and an impurity) in a semiconductor is modified as follows in the presence of the boundary with the metal:

$$V(x) = \pm \varphi(x) - 2V_0,$$

where

$$\varphi(x) = -\frac{e^2}{\epsilon\rho} + \frac{e^2}{\epsilon \sqrt{\rho^2 + 4d^2}}, \quad 2V_0 = \frac{e^2}{2\epsilon d};$$

the upper signs in $V(x)$ pertain to quasiparticles with unlike charges, and the lower signs to the case of like charges. The second term in $\varphi(\rho)$ takes account of the interaction of the quasiparticles with the "unlike" image, and the quantity $-2V_0 = -e^2/2\epsilon d$ describes the attraction of the quasiparticles to their own image, which is independent of the sign of the charge. This attraction may result in a cardinal restructuring of the spectrum of a narrow-band semiconductor near the metal. In fact, the minimum energy required for production of a particle and a hole near the boundary is not 2Δ (2Δ is the width of the forbidden band in the bulky sample), but $2\Delta^{\text{eff}} = 2\Delta - 2V_0$ (the interaction of unbound quasiparticles with one another is immaterial here, since they are, on the average, at infinite distances from one another). At $V_0 > \Delta$, the ground state of a thin film of an intrinsic semiconductor becomes unstable with respect to formation of electron-hole pairs until the increased Fermi energy of the quasiparticles cancels $2V_0 - 2\Delta$. The stable state of the semiconductor corresponds to a semimetal, i.e., a thin

layer of the semiconductor is transformed into a semimetal near the boundary under the action of electrostatic-image forces. Image forces may also initiate a Mott semiconductor-metal transition in a rather broad layer of an impurity semiconductor near a boundary with a metal. This results from significant weakening of the attraction $\varphi(x)$ of the electron to the impurity near the boundary (at $\rho \gg d$, $\varphi(\rho) \sim -2d^2e^2/\rho^3$). The latter results in a significant decrease of the ionization energy of the impurity and an increase in the radius a_0 of the isolated impurity state^[6,7], which makes for satisfaction of the Mott transition criterion $a_0 \lesssim cd$ (d is the distance between impurities, and $c \sim 1$). A similar weakening of the attraction between electrons and holes near the boundary results in a (d -dependent) decrease in the bonding energy of the Wannier-Mott exciton, an increase in its radius, and the disappearance of the excited states^[7]. Self-image attraction results in the formation of a Wannier-Mott exciton that is bound at the boundary (like the SE considered above)^[7].

We note also that weakening of the Coulomb repulsion of electrons (at $\rho \gg d$) in a thin film of degenerate semiconductor bordering on a metal could raise the superconductive-transition temperature in such a film if the pairing interaction is not weakened due to the small effective radius $r \lesssim d$. Such a situation could be realized under certain conditions in certain multi-valley semiconductors^[8].

Above we have considered excited states of metal-dielectric and metal-semiconductor contacts without consideration of electron-state hybridization effects. However, electrons may hop between the two media if the contact is tight. In particular, if the ionization potential of the dielectric molecules is sufficiently small, the molecules are ionized, and it is possible in principle for an electric double layer to form on the boundary^[9]. A two-dimensional ionic crystal of this kind gives rise to new elementary excitations—a surface Born vibrational branch and surface exciton states with charge transfer. The configuration of the layer may change along the boundary, forming an ordered structure that may be restructured by undergoing phase transitions of the type considered in^[10].

If a valence level E_0 of the molecule is situated near the Fermi level E_F of the metal, various new effects appear. In (intramolecular) vibration of the molecule, the level E_0 oscillates around E_F , so that the valence electron enters the metal (at $E_0 > E_F$) and resettles on the molecule by turns. Therefore the charge localized on the molecule oscillates. This results in a specific interaction of the metal's conduction electrons with the intramolecular vibrations^[11]. Analysis of this coupling may prove essential for calculation of the electron-electron pairing constant in thin films of a metal on a dielectric substrate.

Let us now discuss the possible role of the SE considered above in the exciton mechanism of supercon-

ductivity. We stress that their spectrum can, generally speaking, differ cardinally from the bulk-exciton spectrum. A calculation indicates that the electron-attraction constant due to exchange of SE may be considerably larger than that for exchange of bulk excitons, and that the coupling constant λ_S due to the SE becomes larger the more strongly the SE are localized near the boundary. This result is similar to the conclusion of^[3] that the contribution of excitations of large molecules to the coupling constant is ineffective. In particular, we have for SE localized on the molecular layer nearest to the metal $\lambda_S/\lambda_V = \exp(2k_F a) - 1$, where λ_V is the coupling constant due to bulk excitons, k_F is the Fermi momentum, and a is the lattice constant of the molecular crystal.

The above poses the problem of the physicochemical engineering of the structure and properties of a metal-dielectric transitional layer with the necessary spectrum of SE that interact strongly with the conduction electrons of the metal.

In one promising system, a structural phase transition takes place at the interface at low temperatures and is accompanied by the appearance of a soft surface mode, whose presence might tend to raise the temperature of the superconductive transition in a thin layer of the metal.

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