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# *OPTICAL TRANSITIONS BETWEEN CLOSELY SPACED IMPURITY CENTERS AND THE RELATED PHOTOCONDUCTIVITY*

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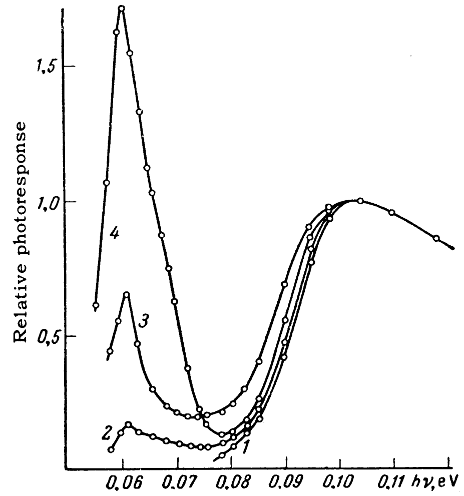


Photoconductivity spectrum of Ge:Zn:Sb. Zinc concentration (in $cm^{-3}$): 1) $1.2 \times 10^{15}$; 2) $1.6 \times 10^{16}$; 3) $4 \times 10^{16}$; 4) $3 \times 10^{17}$. Field 50 V/cm, T = 4.2°K.

If a semiconductor is doped with two types of impurity, giving rise to two different energy levels, then at a sufficiently high impurity concentration, when the wave functions of the impurity states partly overlap, optical tunnel transitions of carriers become possible between nearby impurity centers of different type. We shall assume that the concentration of the centers with the shallower level is high. Therefore, a carrier, which finds itself at one of these centers after an optical transition, can take part in "jump" conduction along these centers. This gives rise to a characteristic photoconductivity. Carriers cross over from one impurity state to another without being transferred to the free bands (the conduction band or the hole band). This phenomenon may be observed also when the necessary two levels are due to a single impurity which may have several charge states.

The effect just described was observed in germanium—doped with zinc and compensated with antimony—at the temperature of liquid helium. Zinc forms two acceptor levels in Ge, which are separated by 0.03 and 0.09 eV from the edge of the valence band. The concentration of zinc in different samples varied from $\approx 10^{14}$ to $3 \times 10^{17}$ $cm^{-3}$. The concentration of antimony was in each case selected so that the 0.03 eV level was completely and the 0.09 eV level partly filled with electrons. The photoconductivity spectra of these samples were measured. The results are shown in the figure, from which it is evident that at zinc concentrations of $\lesssim 10^{15}$ $cm^{-3}$ the spectrum has a shape typical of the impurity photoconductivity due to the photoionization of $Zn^-$.[1] On increasing the zinc concentration, a photoconductivity peak appeared beyond the long-wavelength edge, the maximum of the peak lying at the photon energy of 0.06 eV. The height of the peak rose with the concentration of zinc but its position was not affected.

The appearance of this peak is due to an optical transition of a hole from a $Zn^-$ ion to a nearby similar ion. A second hole of the resultant neutral atom $Zn^0$ wanders along the $Zn^-$ ions and contributes to the jump conduction. A confirmation of this interpretation is provided by the characteristic photoconductivity spectrum (a narrow peak), the exact coincidence of the peak position (0.06 eV) with the difference of the energies of the two zinc levels, the concentration dependence of the height of the peak, the absence (or a very small value) of the photo-Hall effect at the peak, and the presence of a considerable "jump" conduction along the zinc levels.[2]

The effect described cannot be related to an optical transition of a hole to an excited state in the same $Zn^-$ ion because, as shown in [3], there are no optical transitions with the energy $\approx 0.06$ eV inside $Zn^-$ ions in Ge.

It is interesting to note that an increase of the electric field to $\approx 200$ V/cm splits the peak into four components.

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## *ON THE SUPERCONDUCTIVITY OF ELECTRONS AT THE SURFACE LEVELS*

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As far back as 1932[1], 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, [2]) 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[3] 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[1)]

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

we can easily prove that the usual discussion (see, for example, [4]) 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

$$1 = -\frac{\lambda}{2\,(2\pi)^2}\int\frac{d^2p}{\varepsilon_p}. \qquad (2)$$

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

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

On the other hand, in the three-dimensional case, the well-known Bardeen, Cooper, and Schrieffer expression (see [4]) 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 $a \sim 3\times10^{-8}$ 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