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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICS

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ON THE CHANGE OF SIGN OF THE PHOTO-EMF IN ANTHRACENE

(Presented by Academician M. A. Leontovich, 18 XII 1967)

It was shown earlier (1) that anthracene possesses hole conductivity. The magnitude of the photo-emf for thin anthracene crystals with electrolytic electrodes, with an external load of 10^9 Ω, was about 100 mV (2).

In measuring the photo-emf on anthracene we observed an interesting phenomenon which, as far as we know, had not been observed previously. In the region of the fundamental absorption of anthracene ($\lambda < 4000$ Å at $T = 300$°K) we observed the already known course of the photo-emf, according to whose sign anthracene in this region has hole conductivity. The oscillations of the photo-emf in this region are due to the presence of exciton absorption bands.

We investigated the photo-emf in the spectral region where the absorption is insignificant ($\lambda > 4000$ Å at $T = 300$°K), and found that here the photo-emf has the opposite sign. The change of sign of the photo-emf at room temperatures occurs at $\lambda = 4000$ Å.

The spectral dependence of the photo-emf for different temperatures is presented in Fig. 1. It is seen that, with increasing temperature, the change of sign of the photo-emf occurs at greater wavelengths.

Fig. 1

We used anthracene which was purified chromatographically, and then, after 100 passes of zone melting by sublimation in an argon atmosphere, single-crystal plates of thickness 30–50 μ were grown from it and used for measurements. At low temperature the luminescence spectrum of such crystals has an exciton character, which served for us as a criterion of crystal purity.

The measurement of the photo-emf was carried out with an electrometric amplifier with an external load of 10^{12} Ω. The electrodes were SnO_2 films deposited on a quartz substrate; one electrode was semitransparent. The crystal was clamped between two electrodes and was illuminated from the side of the semitransparent electrode, perpendicular to the *ab* plane of the crystal. The radiation source was a GSVL-120 lamp.

The observed effect can be explained on the basis of the following model. It is assumed that the main mechanism of formation of nonequilibrium current carriers (electrons and holes) in anthracene is due to the decay of excitons into an electron and a hole; in this case the spatial distributions of elec-

···electrons and holes in the steady state will be determined by the spatial distribution of excitons*:

$$n = \frac{\tau_e}{\tau_{\mathrm{er}}} n_{\mathrm{e}}; \qquad p = \frac{\tau_p}{\tau_{\mathrm{er}}} n_{\mathrm{e}}, \tag{1}$$

where n, p, n_{e} are, respectively, the concentrations of electrons, holes, and excitons; τ_e, τ_p are the lifetimes of electrons and holes; τ_{er} is the lifetime of excitons with respect to decay into an electron and a hole.

The spatial distribution of excitons was found by us from the solution of the diffusion equation, which has the form

$$\frac{d^2 n_{\mathrm{e}}}{dx^2} - \frac{n_{\mathrm{e}}}{l_{\mathrm{e}}^2} = -\frac{\beta I_0}{D_{\mathrm{e}} l_{\mathrm{p}}} e^{-x/l_{\mathrm{p}}}, \tag{2}$$

where $l_{\mathrm{e}} = \sqrt{D_{\mathrm{e}}\tau_{\mathrm{e}}}$, D_{e}, τ_{e}, β are, respectively, the diffusion length, diffusion coefficient, lifetime, and quantum yield of excitons; l_{p} is the light absorption length; I_0 is the intensity of the incident light; x is the coordinate in the direction of illumination.

The solution of equation (2), in the approximation that the rate of surface annihilation of excitons is less than the diffusion rate, has in the simplest cases the form:

a) $l_{\mathrm{e}} > l_{\mathrm{p}}$

$$n_{\mathrm{e}} = \frac{\beta I_0 l_{\mathrm{e}}}{D_{\mathrm{e}}} e^{-x/l_{\mathrm{e}}} \tag{3}$$

b) $l_{\mathrm{e}} < l_{\mathrm{p}}$

$$n_{\mathrm{e}} = \frac{\beta I_0 l_{\mathrm{e}}^2}{l_{\mathrm{p}} D_{\mathrm{e}}} e^{-x/l_{\mathrm{p}}}. \tag{4}$$

Thus, for $l_{\mathrm{e}} > l_{\mathrm{p}}$ the decay constant of the exciton density is determined by the diffusion length of the excitons, while in the case $l_{\mathrm{e}} < l_{\mathrm{p}}$ it is determined by the absorption length of the incident light.

Usually the lifetime of holes is greater than the lifetime of electrons, which is due to the trapping of electrons by defects (3) during exciton decay. Therefore the hole density in the steady state is, as a rule, greater than the electron density, and a hole type of conductivity is usually realized, with the corresponding sign of the photo-emf. Under conditions where the exciton diffusion length is greater than the light absorption length, ionization of trapping centers by light makes no substantial contribution to the electronic conductivity, since the center of gravity of the trapped electrons is separated from the illuminated surface by a distance of the exciton diffusion length, and the radiation does not reach it.

Under conditions where the light absorption length becomes comparable to and greater than the exciton diffusion length, effective ionization of trapping centers occurs with an increase in the quantum yield of electrons. In this case a change in the type of conductivity and, correspondingly, in the sign of the photo-emf is possible. The model described makes it possible to estimate the exciton diffusion length. The change in sign of the photo-emf at room temperatures (Fig. 1) occurs at $\lambda 4000\,\text{Å}$, when the absorption length $l_\text{p} \approx 4 \cdot 10^{-5}\,\text{cm}$. Hence $l_\text{e} \approx l_\text{p} \approx 4 \cdot 10^{-5}\,\text{cm}$. Assuming that $\tau_\text{e} \approx \tau_\phi \approx 2 \cdot 10^{-8}\,\text{s}$ (4), where τ_ϕ is the fluorescence time of anthracene, we find the exciton diffusion coefficient:

$$D_\text{e} = l_\text{e}^2/\tau_\text{e} \approx 8 \cdot 10^{-2}\ \text{cm}^2/\text{s}.$$

* It is assumed that the diffusion and drift lengths of the current carriers are smaller than the decay constant of the excitons.

Since the diffusion length of the exciton increases with temperature, the passage of the photo-emf through zero should evidently occur with increasing temperature at longer illumination wavelengths, which is also confirmed by experiment (Fig. 1).

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Note: Figure translations are in progress. See original paper for figures.