THE NATURE OF A NEW EFFECT OF A CHANGE IN THE PHOTOCONDUCTIVITY OF ORGANIC SEMICONDUCTORS IN A MAGNETIC FIELD

E. L. FRANKEVICH

Submitted to JETP editor December 15, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) 50, 1226–1234 (May, 1966)

The mechanism is considered of the generation of free charge carriers in a molecular crystal, leading to a dependence of the steady-state photoconductivity on the magnetic field intensity. This mechanism makes it possible to account for all the experimental data on the influence of a magnetic field on the photoconductivity. The main agents of the mechanism are "positronium-like" transport excitons, which are formed from molecular excitons after the absorption of light immediately before the appearance of free carriers. A magnetic field affects the steady-state concentration of transport excitons by mixing the para- and ortho-states with m = 0. It is shown that the effect depends on the ratio of the populations of the ortho- and para-states and on the intensity of the incident light. New results are reported on the quenching of the photoconductivity of an anthracene single crystal in a magnetic field, which are described well by the proposed mechanism.

THE influence of a magnetic field on the value of the photoconductivity of several condensed aromatic compounds (anthracene and tetracene) was discovered[1] in an investigation of the motion of carriers in thin deposited films. The effect consisted of an increase, by several per cent, in the photoconductivity in fields ≈1000 Oe; this increase was independent of the relative orientation of a sample and the magnetic field. Later, the effect was observed also in single-crystal samples of naphthalene and anthracene.[2] In single crystals, the photoconductivity was reduced by the application of a magnetic field and the reduction depended on the orientation of the sample and the magnetic field. Initially this observation was the basis for attributing the effect to some special manifestation of the influence of a magnetic field on the carrier mobility. However, experiments, in which carriers were injected from electrodes and currents were limited by space charge, demonstrated the absence of any influence of a magnetic field on the motion of carriers in deposited films and in single crystals. It was also found that a magnetic field did not change the extinction coefficient of the investigated substances. Thus, the change in the photoconductivity in a magnetic field could have been due to the influence of the field on processes taking place after the absorption of light but before the generation of carriers.

The mechanism of carrier generation by light in molecular crystals has been discussed frequently in the published literature (cf., for example, [3]). It has been reliably established that the process of absorption of light generates excited molecules (singlet excitons). It is regarded as likely that in the next stage carriers are formed by the thermal or impurity dissociation of excitons or by the recombination of excitons. The observed "sensitivity" of the process of carrier generation to the application of a magnetic field throws additional light on this process and makes it easier to understand.

In the present paper, the published experimental results on the influence of a magnetic field on the photoconductivity[1,2] and additional results obtained by the present author are used as a basis of a model which allows us to explain this new effect.

1. PRINCIPAL EXPERIMENTAL DATA

We shall now summarize the experimental data on the new effect, as reported in [1,2].

1. Thin (3–20 μ) films exhibit only an increase in their photoconductivity in a magnetic field (the positive effect). The same effect is observed in an investigation of the surface conductivity in single crystals.

2. The negative effect (a reduction in the photoconductivity) is observed in single crystals when light is absorbed in the surface layers of a sample and optically generated carriers move into its interior.

3. The positive effect is independent of the intensity of illumination.

4. The absolute magnitudes of the positive and negative effects increase as the magnetic field intensity is increased but reach saturation in fields of 1000–3000 Oe.

2. NEW EXPERIMENTAL DATA ON A CHANGE IN THE PHOTOCONDUCTIVITY OF AN ANTHRACENE SINGLE CRYSTAL IN A MAGNETIC FIELD

The change in the photocurrent flowing through an anthracene single crystal was investigated when a magnetic field was applied; this was done at various illumination intensities. We used an anthracene single crystal, 4 × 4 × 1 mm and cleaved along the ab plane. The crystal was investigated in a "sandwich"-type cell. The electrode through which the sample was illuminated was made of glass coated with a transparent film of tin dioxide, which was pressed tightly against the crystal surface. The second electrode was a silver paste deposited on the crystal surface. The same results were obtained when the pressure contact was replaced with a silver paste grid deposited on a crystal. A discharge lamp of the DKSSh-1000 type was used as the source of continuous illumination. The intensity was reduced by means of a set of neutral light filters. The attenuation of light of wavelengths <4000 Å was allowed for. A constant voltage of 300–500 V was applied to the electrodes. The current through a sample was measured with an electrometer amplifier of the U1-2 type: it amounted to 10^{-10}–10^{-7} A. A magnetic field of 3000 Oe intensity, established by means of an electromagnet, was directed along the ab plane of the crystal.

It was found that when the illuminated electrode had positive polarity the photoconductivity was considerably higher than when this electrode was negative, which is in agreement with the published results.[4] When the illuminated electrode was positive, the application of a magnetic field reduced the photoconductivity. When the same electrode was negative, the photocurrent increased by 0.5–1%, which was obviously due to the influence of the surface photoconductivity: when a crystal was illuminated at the open end (light directed parallel to the electrode planes), the application of a magnetic field gave a positive result.

Figure 1 shows an experimentally determined dependence of the relative change in the photocurrent Δi/i, caused by a magnetic field, on the photocurrent i. The photocurrent itself increased

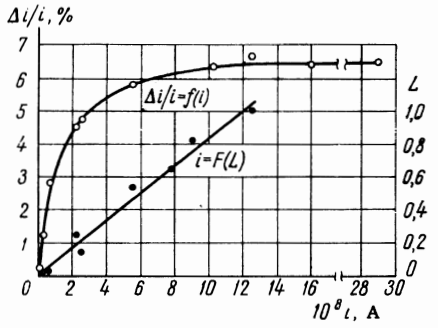

FIG. 1. Dependence of the relative change in the photocurrent on the total photocurrent [curve Δi/i = f(i)]. The dependence of the photocurrent i on the intensity of illumination L is also included: curve i = F(L), where L is in relative units; H = 3000 Oe. "Sandwich"-type cell, voltage across electrodes 300 V.

linearly as the intensity of light was increased [curve i = F(L) in Fig. 1]. At low intensities, a magnetic field had no effect on the photoconductivity. At high intensities of illumination, Δi/i reached saturation. The value of $(\Delta i)_{max}$ was within the range 3–12% and varied from crystal to crystal.

It should be mentioned that the determined dependence of Δi/i on the illumination intensity for the negative effect of the magnetic field differed considerably from the analogous dependence in the positive effect[1] and could be used to check the model describing the nature of the investigated effect.

3. SELECTION OF THE MODEL

In a system of diamagnetic molecules (such as anthracene) illuminated with light, the only particles "sensitive" to a magnetic field are electrons and holes. However, as mentioned in [2], a magnetic field of ~1000 Oe is far too weak to affect the motion of electrons and holes. Also the magnetic moment of electrons and holes can interact with the field. The energy of this interaction is approximately equal to μH, where μ is the Bohr magneton; and in our case, this energy was $\approx 6 \times 10^{-6}$ eV, which was considerably less than kT. This estimate shows that a free electron or hole interacting with the lattice is practically insensitive to a magnetic field of this intensity.

The energy of 10^{-5} eV is comparable only with the spin-spin interaction energy of an electron and a hole and it may play a role in those states in which this interaction is important. In particular, the spin-spin interaction is important in the states in which positive and negative charges (a hole and an electron) are bound by the Coulomb forces. In

the literature on organic semiconductors, such states are usually called transport excitons. A positronium atom is a close analogy of transport excitons. It is known that a magnetic field shortens the lifetime of a positronium atom due to the partial transition of the positronium ortho-states to the shorter-lived para-states.[5] A similar effect can be expected for transport excitons. Thus, the recombination of a hole and an electron, which form a transport exciton, is the equivalent of the annihilation of an electron and a positron.

It should be stressed that light generates molecular excitons in molecular crystals. The formation of transport excitons, which are "positronium-like" states of an electron and a hole, has to be postulated to account for the influence of a magnetic field on the photoconductivity.

The possibility of the presence of transport excitons follows from the fact that the excitation energy of a molecule (for example, anthracene) to the first singlet level is insufficient to form free carriers but it may give rise to a considerable (5–10 Å) increase of the distance between an electron and a hole which are bound by the Coulomb force.

The spectrum of transport excitons in molecular crystals has been discussed theoretically in many papers.[6-8] The lower state in this spectrum corresponds to the transition of an electron from one molecule to a neighboring one. The state formed in this way is usually called a charge-transfer complex. Direct optical transitions to this state have been found experimentally for many two-component organic semiconductors (cf., for example, [9]). These transitions were usually absent in one-component crystals.[8, 10]

To simplify the problem, we shall describe the transport exciton states by the "positronium" eigenfunctions, which will be a good approximation for large distances between a hole and an electron.

Thus, we shall postulate that the formation of a localized exciton $^1S_0$ is followed (probably with a low probability) by the formation of a transport exciton P, which is immediately followed by the generation of free carriers n and p:

$$h\nu + M \rightarrow {}^1S_0 \rightarrow \mathrm{P} \rightarrow n, p.$$

In accordance with the principle of conservation of the spin of a system, the first transport excitons to form will have a total spin equal to zero, i.e., para-excitons will be formed first. Because of their interaction with the lattice, these excitons will then undergo transition to the ortho-state so that at equilibrium the ratio of the ortho- and para-state populations of transport excitons will be governed by their statistical weights and lifetimes.

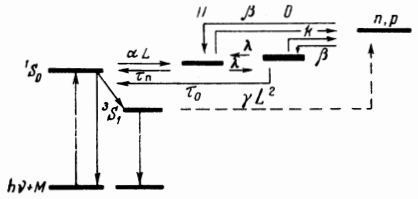

FIG. 2. Scheme of transitions between excited and ionized states during the absorption of light. The symbols are explained in the text.

Figure 2 shows a scheme of states and transitions which is used as the model in the present investigation. Here $^1S_0$ represents localized singlet excitons formed by the action of light, P and O represent the para- and ortho-states of transport excitons, while n and p are free charge carriers.

The scheme in Fig. 2 gives the transition rate constants and the excited-state lifetimes essential for the calculation of the relative population of the ortho- and para-states of transport excitons: α is the rate of generation of transport para-excitons when the intensity of light is equal to unity; since transport excitons are formed from singlet excitons $^1S_0$, α is governed by the probability of formation of an exciton and the probability of its transition to P; τ_p is the lifetime of a para-exciton before recombination; τ_o is the lifetime of an ortho-exciton; λ is a constant representing the rate of transitions between the para- and ortho-states, governed by the interaction with the lattice; k is a constant representing the rate of dissociation of transport excitons to form free charge carriers; β is a constant representing the recombination velocity of free carriers; when these carriers recombine, they again form transport excitons. We shall not consider the mechanisms of the various transitions. The only important fact to note is that the rate of formation of free carriers is governed by the total concentration of transport excitons.

4. INFLUENCE OF A MAGNETIC FIELD ON THE TOTAL POPULATION OF ORTHO- AND PARA-STATES OF TRANSPORT EXCITONS

Transport excitons in the ortho- and para-states can be described by the ψ-functions, $\psi_{1,\pm1}$, $\psi_{1,0}$, and $\psi_{0,0}$, which are the solutions of Schrödinger's equation with the potential $U(r) = -e^2/\epsilon r$, where ϵ is the permittivity of the medium. The subscripts of the ψ-functions denote, respectively, the total magnetic moment and the projection of the magnetic moment.

The positions of the lower excited states of the ortho- and para-excitons differ from one another by the energy ΔW of the spin-spin and exchange interactions.

A magnetic field produces the Zeeman effect in the ortho-state by lifting the degeneracy of the magnetic quantum number (m). Moreover, a magnetic field mixes the para-state with the ortho-state having m = 0. In a magnetic field, the functions $\psi_{1,0}$ and $\psi_{0,0}$ are replaced by the functions

$$U_{1,0} = \frac{1}{\sqrt{1+a^2}}\psi_{1,0} + \frac{a}{\sqrt{1+a^2}}\psi_{0,0},$$

$$U_{0,0} = \frac{1}{\sqrt{1+a^2}}\psi_{0,0} - \frac{a}{\sqrt{1+a^2}}\psi_{1,0},$$

where $a = g\mu H/\Delta W$.[10]

If, in the absence of a magnetic field, the rate of filling of the state $\psi_{1,0}$ is A and the rate of filling of the state $\psi_{0,0}$ is B, then, in the presence of a field, the corresponding rates of filling of the states $U_{1,0}$ and $U_{0,0}$ are $A' = A(1-x^2) + Bx^2$ and $B' = Ax^2 + B(1-x^2)$, where x denotes the quantity $a/\sqrt{1+a^2}$. The concentrations n_{U_1} and n_{U_0} in the filled states $U_{1,0}$ and $U_{0,0}$ are given by the equations

$$\frac{dn_{U_1}}{dt} = A(1-x^2) + Bx^2 - \frac{n_{U_1}(1-x^2)}{\tau_0'} - \frac{n_{U_1}x^2}{\tau_p'},$$

$$\frac{dn_{U_0}}{dt} = Ax^2 + B(1-x^2) - \frac{n_{U_0}(1-x^2)}{\tau_p'} - \frac{n_{U_0}x^2}{\tau_0'}.$$

The solutions of these equations under steady-state conditions gives the following expressions for n_{U_1} and n_{U_0}:

$$n_{U_1} = \frac{A(1-x^2)+Bx^2}{(1-x^2)/\tau_0' + x^2/\tau_p'},$$

$$n_{U_0} = \frac{Ax^2+B(1-x^2)}{(1-x^2)/\tau_p' + x^2/\tau_0'}.$$

If, in the absence of a magnetic field, the steady-state concentrations of the states $\psi_{1,0}$ and $\psi_{0,0}$ are, respectively, n_{ψ_1} and n_{ψ_0}, then, obviously, in a magnetic field

$$n_{U_1} = \frac{n_{\psi_1}\tau_p'(1-x^2) + n_{\psi_0}\tau_0'x^2}{(1-x^2)\tau_p' + x^2\tau_0'}, \quad (1)$$

$$n_{U_0} = \frac{n_{\psi_1}\tau_p'x^2 + n_{\psi_0}\tau_0'(1-x^2)}{(1-x^2)\tau_0' + x^2\tau_p'}, \quad (2)$$

where τ_p' and τ_0' are the effective lifetimes of the para- and ortho-excitons, which govern their steady-state concentrations.

We shall not be interested in the dependence of the total population of the transport exciton states with m = 0 on x (on magnetic field). (The states with m = ±1 are not affected by a magnetic field and their populations remain constant if one can neglect transitions between the ortho-exciton sublevels having different m.) The change in the population Δn is given by the formula $\Delta a = n_{U_1} + n_{U_0} - n_{\psi_1} - n_{\psi_0}$. Introducing the notation $\tau_p'/\tau_0' = \xi$, $n_{\psi_1}/n_{\psi_0} = \eta$, and bearing in mind that $\xi \ll 0$, we obtain for Δn:

$$\Delta n = n_{\psi_0}x^2(1-\eta)/(\xi + x^2).$$

From Eq. (3) it follows that

$$\Delta n = 0, \quad \text{if} \quad \eta = 1;$$

$$\Delta n < 0, \quad \text{if} \quad \eta > 1;$$

$$\Delta n > 0, \quad \text{if} \quad \eta < 1.$$

The same equation can also be expressed in terms of $a = g\mu H/\Delta W$:

$$\Delta n / n_{\psi_0} = a^2(1-\eta)/(a^2+\xi). \quad (4)$$

Since transport excitons govern the generation of carriers ($i \propto n^{1/2}$), the changes in the photocurrent due to the application of a magnetic field are $\Delta i \propto \Delta n$ and $\Delta i/i = \Delta n/4n_{\psi_0}$.

Figure 3 shows the dependence of $\Delta n/n_{\psi_0}$ on a calculated from Eq. (4) for various values of the parameters η and ξ. From these curves it is evident that the highest values of $\Delta n/n_{\psi_0}$ are $1-\eta$; the lower the value of the ratio $\tau_p'/\tau_0' = \xi$, the lower the values of a at which $\Delta n/n_{\psi_0}$ reaches saturation. The shape of the calculated curves is similar to the experimentally observed dependences of $\Delta i/i$ on the magnetic field.[1,2] The experimental curves of $\Delta i/i = \Delta n/4n_{\psi_0} = f(H)$ can be used to find the parameter η, which is

$$\eta = 1 + 4|\Delta i/i|_{max}$$

and the quantity

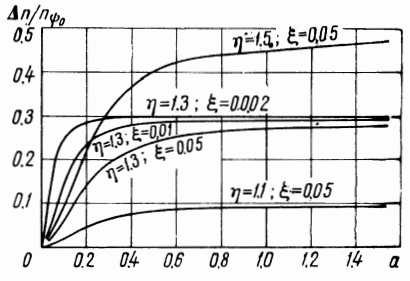

FIG. 3. Dependence of the relative reduction in the concentration of transport excitons $\Delta n/n_{\psi_0}$ in a magnetic field on $a = g\mu H/\Delta W$, calculated from Eq. (4). Curves are given for different values of the parameters η and ξ.

$$\xi\left(\frac{\Delta W}{g\mu}\right)^2 = H^2\left[\left|\frac{|\Delta i/i|_{max}}{|\Delta i/i|} - 1\right]\right];$$

to determine the value of ξ, it is essential to have independent information on the magnitudes of the spin-spin and exchange interactions ΔW.

The positive effect curves (for $\eta < 1$) resemble the curves for the negative effect; when x increases, $\Delta n/n_{\psi_0}$ tends to the value $1 - \eta$.

Thus, summarizing, we can say that the magnetic field can alter the concentration of transport excitons if the steady-state concentrations of the para- and ortho-excitons with m = 0 are not equal.

5. STEADY-STATE CONCENTRATIONS OF TRANSPORT EXCITONS OF THE ORTHO- AND PARA-TYPE

The concentrations of transport excitons and of electrons formed by the dissociation of these excitons are, according to the scheme shown in Fig. 2, given by the equations

$$\frac{dn_{\psi_0}}{dt} = \alpha L - 3\lambda n_{\psi_0} - \frac{n_{\psi_0}}{\tau_p} + 3\lambda n_{\psi_1} + \beta n^2 - k n_{\psi_0}, \quad (5)$$

$$\frac{dn_{\psi_1}}{dt} = \lambda n_{\psi_0} - \frac{n_{\psi_1}}{\tau_0} - \lambda n_{\psi_1} + \beta n^2 - k n_{\psi_1}, \quad (6)$$

$$\frac{dn}{dt} = k(3n_{\psi_1} + n_{\psi_0}) - 4\beta n^2. \quad (7)$$

The solution of Eqs. (5), (6), and (7) under steady-state conditions gives

$$\eta = \frac{n_{\psi_1}}{n_{\psi_0}} = \frac{\lambda + k/4}{1/\tau_0 + \lambda + k/4}. \quad (8)$$

The condition $1/\tau_0 \ll (\lambda + k/4)$ is very interesting because then the last equation gives $\eta = 1$, i.e., equal populations of the states $\psi_{0,0}$ and $\psi_{1,0}$.

Under real conditions, the equality of the populations of the states $\psi_{0,0}$ and $\psi_{1,0}$ may not be obtained. Thus, in thin films, we can expect a reduction in the intrinsic lifetime of ortho-excitons τ_0 because of their annihilation (or dissociation into carriers) at the surface of the film (or on electrodes in "sandwich"-type samples). The reduction in τ_0 leads, as indicated by Eq. (8), to a decrease in η and a consequent increase in the photoconductivity in a magnetic field.

However, the reduction in the exciton lifetime can give rise only to the positive effect. To explain the negative effect, we need an independent source of population of the ortho-states. In the presence of such a source, the concentration of the ortho-excitons should increase because of their relatively long lifetime. The sources of the ortho-excitons are the para-states and the recombination of free electrons and holes. However, according to the assumed scheme, the carriers themselves are formed by the dissociation of excitons, so that the population of the ortho-states is equivalent to an increase in the rate of exchange between the ortho- and para-states, leading to $\eta = 1$.

It follows from this discussion that the existence of a source of carriers independent of transport excitons will lead to a preferential population of the ortho-states. Such a source may be the recombination of singlet excitons formed initially by the action of light or the recombination of triplet excitons, which are present in a much higher concentration. This source of free carriers is denoted by a dashed line in Fig. 2. If the rate of generation of carriers in the case of recombination of molecular excitons is γL^2, where γ is a coefficient of proportionality governed by the absorption coefficient of light and the lifetime of molecular excitons, then an allowance for an additional source of carriers alters Eq. (7) for η, when $1/\tau_0 \ll (\lambda + k/4)$, to the form

$$\frac{1}{\eta} = 1 - \frac{1}{4}\frac{\gamma L^2}{\tau_p}\left[\alpha L\left(\lambda + \frac{k}{4}\right) + \gamma L^2\left(\lambda + \frac{1}{4}\frac{1}{\tau_p} + \frac{k}{4}\right)\right]^{-1} \quad (9)$$

In magnetic fields of high intensity, the variation of η with L corresponds to an increase in the relative change in the photocurrent, expressed by the following formula

$$\frac{\Delta i}{i} = \frac{1}{4}(\eta - 1) \approx \frac{1}{16}\frac{\gamma L^2}{\tau_p}\left[\alpha L\left(\lambda + \frac{k}{4}\right) + \gamma L^2\left(\lambda + \frac{1}{4}\frac{1}{\tau_p} + \frac{k}{4}\right)\right]^{-1}. \quad (10)$$

This formula is valid when $k \gg \lambda$. The dependence $\Delta i/i$ on L has a form similar to that observed experimentally for anthracene single crystals (Fig. 1). The dependence $\Delta i/i = f(L)$ calculated from Eq. (10) can be made to coincide with the experimental curve (Fig. 1) by a suitable selection of the parameters. As $L \to \infty$, the ratio $\Delta i/i$ tends to a constant value, which is

$$\left[16\tau_p\left(\lambda + \frac{1}{4}\frac{1}{\tau_p} + \frac{k}{4}\right)\right]^{-1}.$$

It should be mentioned that direct filling of the transport exciton states by the recombination of molecular excitons leads to a similar expression.

CONCLUSIONS

The proposed model describes satisfactorily all the principal features of the influence of a mag-

netic field on the photoconductivity. Within the framework of this model, we can explain the anisotropy of the effect of the magnetic field in single crystals, detected in [2] and evidently associated with the anisotropy of the effective carrier mass. The known dependence of $\Delta i/i$ on the electric field intensity[2] is also a natural consequence of the model: an increase in the field intensity in the region of carrier generation gives rise to a greater separation between positive and negative carriers and, by reducing the number of recombinations, reduces the rate of nonuniform filling of the ortho-states.

In the present paper, we have not considered the mechanisms of the transitions between various states the former of which end in the formation of free carriers. Since the free-carrier level lies above the singlet level of molecular excitons,[8] it is quite likely that carriers are generated by the recombination processes in which transport excitons participate. The generation of carriers in these processes predominates at low intensities of illumination, probably because of the long lifetimes of transport excitons, compared with molecular excitons.

Further investigations of the change in the photoconductivity in a magnetic field will make it possible to investigate in greater detail the role of transport excitons in the generation of carriers. Particularly important is the search for transitions between the $m = \pm 1$ and $m = 0$ states of the ortho-excitons in single crystals subjected to a magnetic field. These transitions, caused by emission in the microwave range, should give rise to additional quenching of the photoconductivity. Detection of these transitions will make it possible to determine the magnitudes of the spin-spin and exchange interactions in transport excitons.

The author is very grateful to Professor A. S. Kompaneets and Professor V. I. Gol'danskiĭ for valuable discussions.

[1] E. L. Frankevich and E. I. Balabanov, JETP Letters **1**, No. 6, 33 (1965), transl. **1**, 169 (1965).

[2] E. L. Frankevich and E. I. Balabanov, FTT **8**, 855 (1966), Soviet Phys. Solid State (in press).

[3] Sang-Il Choi and S. A. Rice, J. Chem. Phys. **38**, 366 (1963).

[4] J. Kommandeur and W. G. Schneider, J. Chem. Phys. **28**, 582 (1958).

[5] V. W. Hughes, S. Marder, and C. S. Wu, Phys. Rev. **98**, 1840 (1955).

[6] R. E. Merrifield, J. Chem. Phys. **34**, 1835 (1961).

[7] Sang-Il Choi, J. Jortner, S. A. Rice, and R. Silbey, J. Chem. Phys. **41**, 3294 (1964).

[8] D. R. Kearns, J. Chem. Phys. **41**, 581 (1964).

[9] A. N. Terenin, Uspekhi khimii **24**, 121 (1955).

[10] R. S. Berry, J. Jortner, J. C. Mackie, E. S. Pysh, and S. A. Rice, J. Chem. Phys. **42**, 1535 (1965).

Translated by A. Tybulewicz
149