

# Dipole charge-carrier capture centers in organic crystals

A. K. Kadashchuk, N. I. Ostapenko, Yu. A. Skryshevskii, V. I. Sugakov,  
and M. T. Shpak

*Institute of Physics, Academy of Sciences of the Ukrainian SSR*

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Shallow carrier capture centers have been observed experimentally in molecular crystals. The capture centers result from a constant dipole moment of an impurity. A capture center arises as a result of interaction of the dipole moment of the impurity with a carrier which is localized at an adjacent molecule in the crystal.

The nature of the shallow carrier trapping centers which are induced by impurities in organic crystals is unknown, and there have been exceedingly few studies of these centers.<sup>1</sup> The situation here is radically different from that of semiconductors, in which the positions of the levels of shallow donors and acceptors can be predicted. On the other hand, in order to produce organic crystals with a given conductivity, it is necessary to add an impurity which creates capture centers of a certain depth, which determine the magnitude and temperature dependence of the mobility. In an effort to identify the possible types of capture centers in organic crystals, we have undertaken a systematic series of experiments on systems for which a model of the capture centers can be predicted and calculated.

These systems are molecular crystals with impurities whose molecules have a constant dipole moment. In this case, a trapping center may arise as a result of interaction of a charge carrier with the dipole moment of the impurity. The carriers are localized at the crystal molecules closest to the impurity, and the magnitude of the dipole moment of the impurity determines the depth of the trapping center. If the state formed as a result of this interaction is to have the lowest energy and to be stable, an impurity center must not form for the given type of charge carrier in the crystal. This situation can be arranged for hole and electron trapping centers, respectively, if the ionization potential of the impurity molecule is higher than, and the electron affinity lower than, that of the crystal molecule.

For some experiments on dipole carrier trapping centers we used anthracene crystals with various aromatic and heterocyclic impurities, with dipole moments which varied over the interval  $p = 0-4$  D. To determine the depth of the carrier trapping centers in these systems, we used a thermoluminescence method, which can be summarized as follows. The impurity crystals are illuminated with the light from a DRS-500M mercury-vapor lamp at  $T = 4.2$  K. The samples are then heated at a constant rate of 0.1 K/s. The thermoluminescence signal is detected by an FEU-106 photomultiplier. The resulting thermoemission curves are analyzed by the method of the total thermoemission curve.<sup>2</sup> The error in the determination of trap depths is 10%.

It was found that in pure crystals and also in crystals with impurities with a zero dipole moment no thermoluminescence signal was observed. When the dipole moment

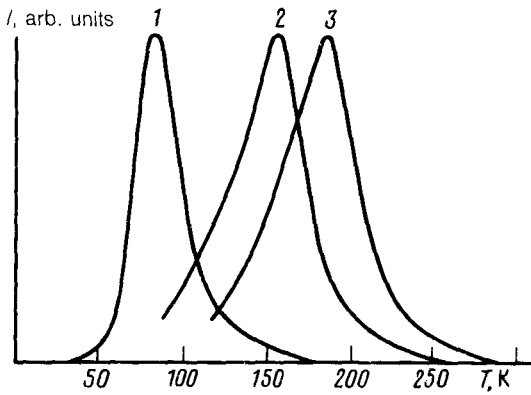


FIG. 1. Curves of the thermoemission of anthracene crystals with several impurities. 1—Carbazole; 2—xanthone; 3—maleic anhydride.

of the impurity was nonzero, the thermoemission curve exhibited an isolated band, whose position along the temperature scale depended on the dipole moment of the impurity. Figure 1 illustrates the results with thermoemission curves of several doped anthracene crystals. A study of the spectrum of the thermoemission of a system of anthracene with a carbazole impurity shows that the emission maximum is at 450 nm, possibly because of a luminescence of anthraquinone<sup>3</sup> in the anthracene. This luminescence may cause an extrinsic photogeneration of carriers in anthracene.<sup>1</sup>

Figure 2 shows the trap depths found from the thermoemission curves versus the impurity dipole moment<sup>4</sup> for several impurities. A shallow trapping center in anthracene with a carbazole impurity, which does not produce an impurity trap, was observed in Ref. 5 by another method, from the temperature dependence of the electron mobility; its depth was found to be 0.034 eV. The depth (0.03 eV) which we observe for the trap in this system agrees with that other figure. Accordingly, the trapping center observed in Ref. 5 can also be interpreted as a dipole trapping center. The impurity trap of acridine for electrons in an anthracene crystal, which was observed in

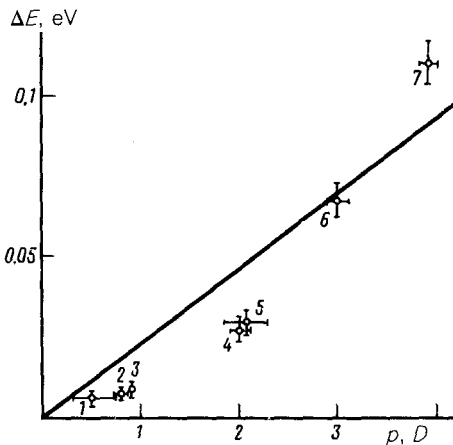


FIG. 2. Depth of the carrier trapping centers in anthracene versus the dipole moment of the impurity. 1—Fluorene; 2—dibenzothiophene; 3—dibenzofuran; 4—acridine; 5—carbazole; 6—xanthone; 7—maleic anhydride. The solid line was calculated from Eq. (2). The horizontal bars represent the scatter in the data on dipole moments in the literature; the vertical bars reflect the error in the determination of the trap depths by this method.

Ref. 6, is at 0.2 eV. The depth of the dipole trap produced by acridine in anthracene (Fig. 2) is 0.024 eV, i.e., an order of magnitude smaller. In this case, therefore, a hole localizes at the shallow trapping center. This conclusion is supported by the circumstance that since the ionization potential of the acridine molecules is higher than that of the anthracene molecules, no impurity hole traps will form in the crystal, so that only traps of a dipole type can arise for holes. In all the systems which we studied, the ionization potentials of the impurity molecules were higher than that of anthracene molecules,<sup>7</sup> so that holes could be trapped only by dipole trapping centers.

The widths of the conduction band in organic crystals are small (on the order of 0.1 eV; Ref. 1). Accordingly, for the molecules closest to the dipole the matrix elements for the transition of an electron between molecules are significantly smaller than the change in the energy of the interaction of the carrier with the dipole. In a calculation of the trap depth  $\Delta E$ , the charge carrier can therefore be regarded as localized at one of the molecules of the crystal closest to the impurity. A rigorous calculation requires consideration of the polarization of the medium, the discrete nature of the lattice, data on the position of the impurity molecule in the lattice, and the charge distribution at the molecule. For estimates we can use the very simple expression

$$\Delta E = \frac{epR}{\epsilon R} \quad (1)$$

where  $\epsilon$  is the dielectric constant of the crystal,  $R$  is the distance between the dipole and the crystal molecule, and  $e$  is the charge of an electron. When the dipole is oriented along the short axis of the molecule, and when the electron is localized at a crystal molecule in another sublattice with respect to the impurity molecule, we find the depths of the dipole trapping centers in the anthracene crystal to be

$$\Delta E = 0.024p \text{ eV}, \quad (2)$$

where  $p$  is expressed in debyes. The  $p$  dependence of  $\Delta E$  found from this formula (the solid line in Fig. 2) agrees with the experimental values, despite the simplified nature of the model on which the calculations were based.

The results of these studies show that the model of a dipole trapping center in organic crystals is correct and can be used to predict the position of levels and the sign of the charge carriers. This model can be used to produce trapping centers with a given depth in a crystal by choosing impurities with a certain dipole moment.

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Translated by Dave Parsons