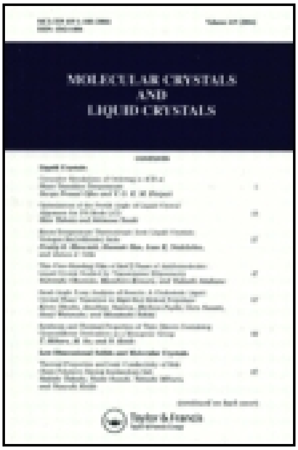

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Clusters of Dipole Charge-Carrier Capture Centers in Organic Crystals

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Clusters of dipole charge-carrier capture centers were studied in anthracene crystals doped with carbazole. The microscopic model for the dipole centers of the different structure is proposed. The thermoluminescence of the anthracene crystal doped with carbazole was investigated in the temperature range of 4.2-300 K. It was shown that thermoluminescence bands became structured with the increase of the impurity concentration. The observed structure is explained by the emergence of dipole charge-carrier capture centers created by clusters of impurities, which consist of one, two or more molecules. The authors carried out theoretical calculations both for immobile carriers and taking into account their delocalisation. The theoretical results are in good agreement with experimental ones.

INTRODUCTION

There is an extremely small number of models of a charge-carrier trap brought about by an impurity that is understandable on the microscopic level for organic crystals as compared with the non-organic semiconductors. The exception is the model of the impurity trap, in which the trap depth can be understood with the aid of the ionization potential value of the impurity.[1] The model of the "dipole" trap for organic cystals was proposed and experimentally corroborated.[2] The formation of these traps is brought about by the interaction of the impurity dipole moment with the charge-carrier. Due to the narrowness of the conduction band the charge-carrier is localized at one of the molecules of the crystal adjacent to the impurity.

The possibility of the charge-carrier localization at the dipole center formed by the magnesium ion and the cationic vacancy (Mg-V) in the crystal LiF_2:Mg and as well as at clusters of these formations was shown earlier.[3] The calculation of the positions of levels and the identification of the structure were not carried out. However, in molecular crystals the cluster trap can have peculiarities connected with the strong anisotropy of the system and extremely narrow conduction band.

In this paper the dependence of the energy spectra of the trap on the concentration of impurities possessing a dipole moment has been studied and also the calculations of the different structure of trap centers have been carried out. The observed structure is explained by the formation of dipole trap clusters.

EXPERIMENT

Anthracene crystals doped with carbazole were chosen for investigations. Sample materials have been refined by means of zone refining (more than 100 zones were used). The dopant concentration was checked by the source material weight and varied from 0.3 to 5%.

The investigations of charge-carrier capture centers in the doped anthracene crystals were carried out applying the thermostimulated luminescence (TSL) technique in the temperature range 4.2-300 K. The thermoluminescence was excited by the UV light. After the irradiation specimens were heated up with the constant velocity 0.1 K/s to obtain glow curves (GC).

The energy spectrum of charge-carrier traps was studied by means of the fractional glow technique (FGT). This method consists of the repeated cyclic heating-up and cooling of the specimen. The mean activation energy E_{eff} was measured in each cycle from the slope of the thermoluminescence intensity increase line, which was drawn in Arrhenius coordinates. The mean temperature T was assigned to each temperature interval of the E_{eff} calculation. It was discovered that the periodicity of the E_{eff} change was 1 K. It should be noted that exact values of the activation energy in the case of the complex structure of thermoluminescence bands can be obtained only by the means of modulated heating, as it is done in the present paper.

Traditional methods of GC processing according to their shape cannot give the detailed information about the trap spectrum because they are based on the assumption that the capture level is single. Glow curves of anthracene crystals doped with carbazole in different concentrations are presented in Figure 1. In the case of relatively low concentration ($c = 0.3\%$) the well defined band in the range of 30 K dominates GC. With the concentration growth more high-temperature bands appear on the thermoluminescence spectrum in the region of 40–65K. The temperature increase leads to the increase of the intensity of these bands and the relative decrease of the intensity of the band near 30 K (see Figure 1).

On Figure 2, bars mark carrier capture levels, which can be obtained by the fractional glowing (0.053; 0.082; 0.102; 0.123 and 0.164 eV). These levels form plateaus on the E_{eff} (T) curve. The designated levels correspond to the temperature maxima on the glow curves of these crystals and correlate with the behavior of

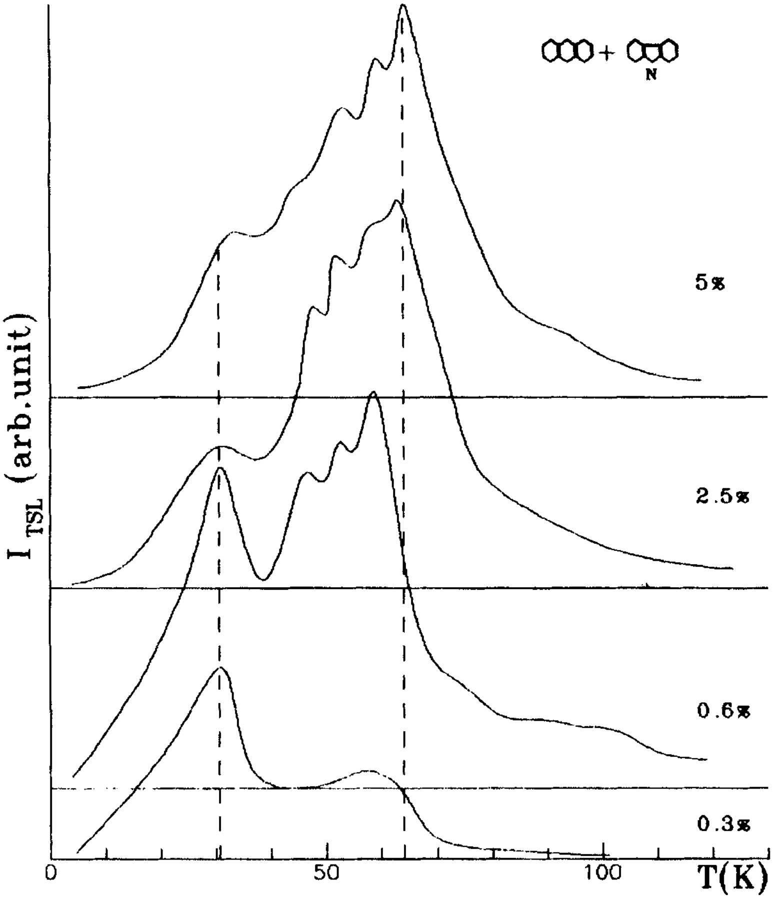


FIGURE 1 The glow curve of the anthracene crystal doped with carbazole.

glow peaks when the impurity concentration increases. With the concentration growth, more deep traps appear, but most of shallow traps exist at any concentration.

CALCULATION AND DISCUSSION

As was shown earlier[2] the carbazole dopant in the anthracene creates a "dipole" trap for holes. The carbazole molecule behaves as an antitrap for the charge-carriers. This is connected with the fact that its ionization potential value is greater than that for anthracene molecule.[1,5] The calculation[6] and some indirect experimental data[1] show, that the electron affinity is less than 0.1 eV, which is less than for the anthracene molecule. Let us note that the shallow electron capture center with the depth 0.034 eV created by the carbazole dopant in the anthracene crystal, which was also observed earlier according to the temperature dependence of the

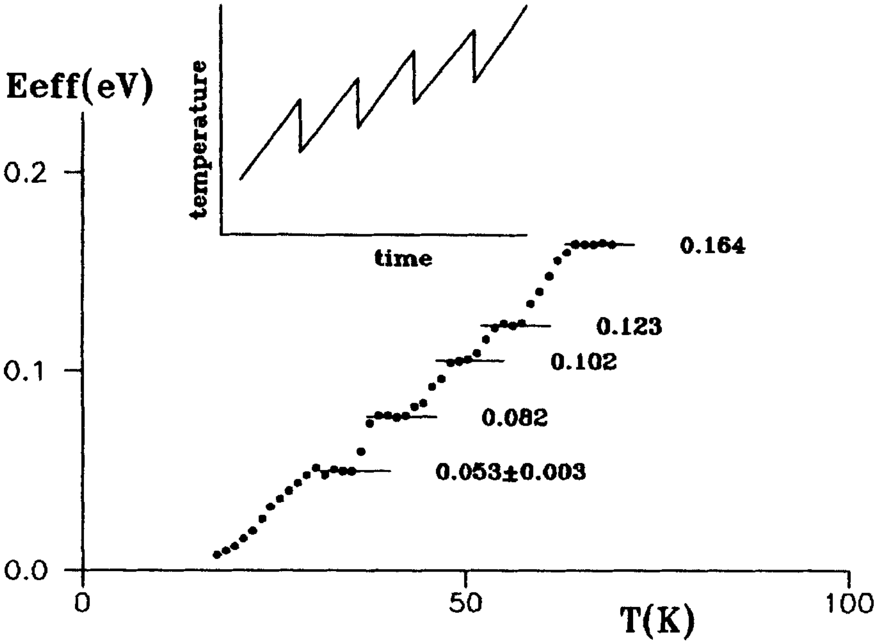


FIGURE 2 The energy spectrum of the anthracene crystal doped with carbazole ($c = 5\%$).

electron mobility,[7] was connected with the perturbing influence of the dopant. However, the nature of perturbation and the microstructure of this center remained unknown.

The structure of the energy spectrum observed in this work can be explained by creation of clusters of dipole traps at the higher dopant concentrations. The single capture centers mainly were observed at the low concentration. The probability for the dopant molecules to be situated more closely and to form complex dipole capture centers increases with the dopant concentration. Within the framework of the model of the immobile charge the determination of the trap depth reduces to the calculation of the energy of interaction between the charge-carrier and the dopant dipoles for different concentrations of dopant, different arrangements of the carrier and dopant and different dipole moment orientations:

$$E = \sum V_{n\alpha} \tag{1}$$

$$V_{n\alpha} = \sum_{\substack{m \neq n \\ \beta \neq \alpha}} \frac{e\vec{p}_{m\beta}\vec{r}_{n\alpha,m\beta}}{\varepsilon r^3_{n\alpha,m\beta}} \tag{2}$$

Here $\vec{r}_{n\alpha,m\beta}$ is the radius vector connecting the carrier, which is situated at the molecule $n\alpha$, with the dipole at the molecule $m\beta$; $\vec{p}_{m\beta}$ is the dipole moment; ε is the dielectric constant of the crystal; e is the charge of the charge-carrier; n is the position of the cell and α is the number of the molecule in the cell.

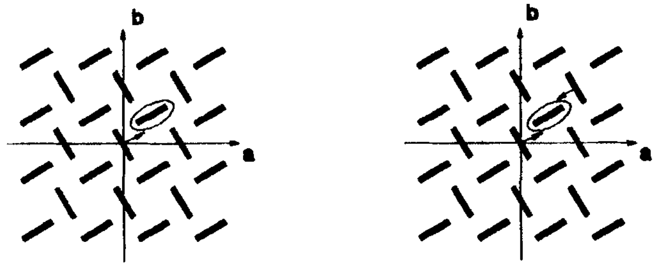
The summation is conducted taking into consideration all dopant molecules in the cluster. The sum is absent for the single center.

The examples of the disposition for single, pair and triple clusters are presented in Figure 3. It was suggested in the calculation that the dipole is oriented along the short axis of the molecule, it has angles with the axes *a*, *b*, *c* of the anthracene crystal: 71.3; 26.6 and 71.8 degrees (position I) or is oriented along the opposite direction (position II), respectively

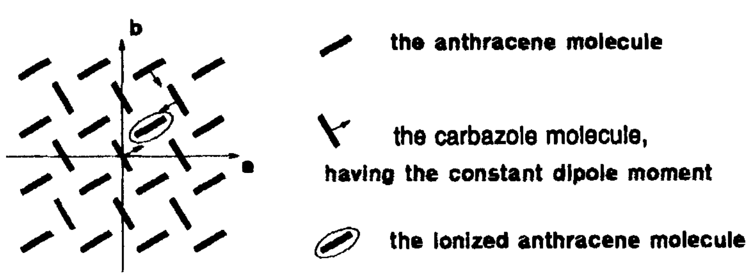
The results of the calculation of the trap depth by the formula (1) are presented in Figure 4 for the clusters with the closest disposition of dopant molecules. The arrangement of levels of capture centers, which were found experimentally by the fractional glow technique, are also given in the same place.

Let us compare the calculated values of the trap depth with the experimental data.

As was found above, the level with the energy of 0.053 eV corresponds to the state when the charge-carrier is localized near the single dipole dopant. The peak on the glow curve at T = 30 K is the most intensive at low dopant concentrations and corresponds to this state. The arrangement of dopant molecules and the ion for the single dipole center is shown in Figure 3a. The calculated value of the trap depth is 0.056 eV in this case and that is close to the observed value.



3a The single center 3b The pair center



3c The triple center

FIGURE 3 The examples of the mutual arrangement of the dipoles and immobile charge-carrier.

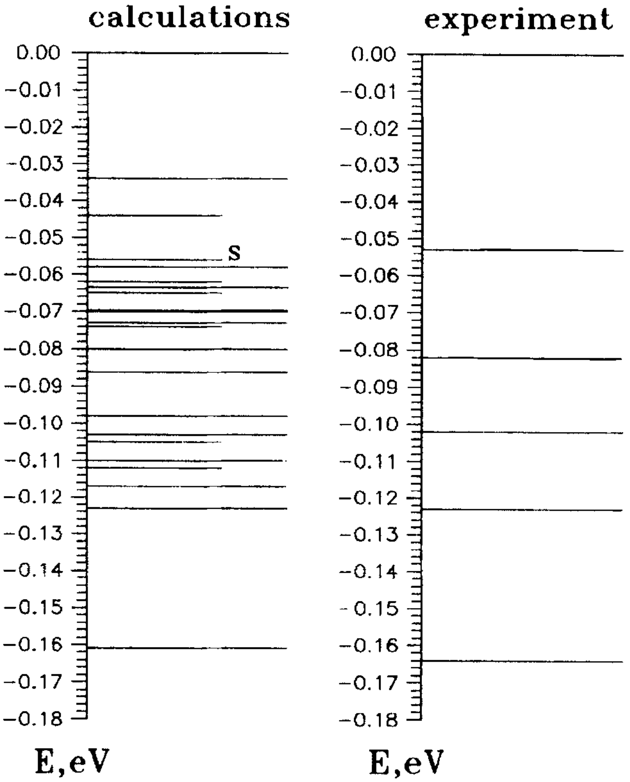


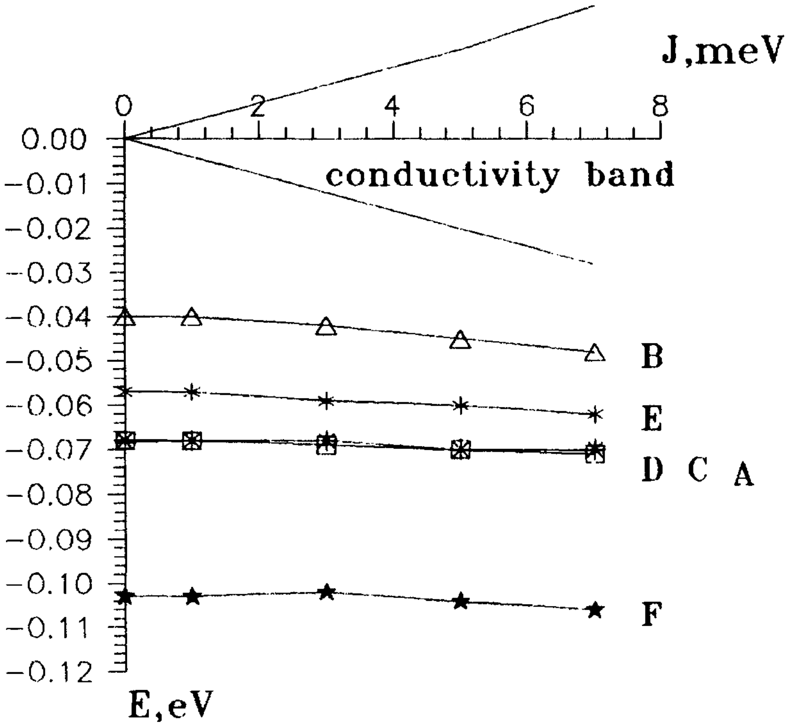
FIGURE 4 The energy spectrum for different types of traps for case of immobile charge-carrier. Longer lines correspond to the triple centers. S = energy of the single center.

The level with the energy of 0.102 eV is intensive at higher concentration of dopant, it corresponds to the charge-carrier localization in the vicinity of two dopant molecules. The deepest calculated level obtained in this case takes place, when the two dipoles are oriented in mutually opposite directions and are placed in the lattice as is shown in Figure 3b. According to (1) the trap depth is equal 0.112 eV for this arrangement.

The cluster shown in Figure 3c has the deepest level for the system of three molecules. Its trap depth is 0.161 eV. It is obvious that the experimental peak on glow curves with the activation energy of 0.164 eV, which is observed at large dopant concentration (c = 5%), corresponds to this state.

We cannot compare the other observed peaks with the cluster model due to the close disposition of levels formed by different clusters. The distance between levels is both within the experimental error and the error of the calculation which is determined by the simplicity of the model and by the inaccuracy of the data about the dipole moment of the carbazole in the anthracene (its magnitude fluctuates from 2.09 to 2.28 debyes according to the different authors).[8]

The multitude of clusters forming levels higher than that of single center exists



	coordin.of the second dipole	direction of its dipole moment
A	1,0	I
B	1,0	II
C	0,1	I
D	0,1	II
E	1,1	I
F	1,1	II

FIGURE 5 The trap depth dependence on element of resonant interaction J in case of twin centers (p = 2.09 D). Coordin. = coordinates x, y.

in the system, but as far as they were not observed in the experiment, we did not pay much attention to them.

We took into account the influence of the motion of charge-carriers on the position of the trap depth. The carrier's movement means that the wave function of the ion is extended over some region near the cluster. The wave function of the charge-carrier localized near the cluster in the approximation of tight coupling may be represented as follows:

$$\psi = \sum_{n\alpha} c_{n\alpha} a^{+}_{n\alpha} | O >, \tag{3}$$

where $a^{+}_{n\alpha}$ is the creation operator of the charge-carrier on the molecule $n\alpha$.

The Schrödinger equation for the wave function (3) may be written as follows:

$$\sum_{\substack{m \neq n \\ \beta \neq \alpha}} J_{n\alpha,m\beta} C_{m\beta} + V_{n\alpha} C_{n\alpha} = E C_{n\alpha}, \tag{4}$$

where $J_{n\alpha,m\beta}$ is the matrix element of resonance interaction between molecules $n\alpha$ and $m\beta$; $V_{n\alpha}$ is the potential energy of the charge-carrier placed at the lattice site $n\alpha$ interacting with all molecules of the crystal according to the formula (1).

We assumed that the matrix element $J_{n\alpha,m\beta}$ is not equal to zero except for adjacent molecules in nonequivalent sites (see Figure 5). The level depth is determined by the distance between the conduction band bottom and the local level. The trap depth contains the linear part with regard to J, because of the conduction band bottom drop with the increase of J. However, the charge-carrier movement contribution to the position of level is small for the anthracene in which J is approximately 10^{-3} eV.[9] The corrections brought about by this contribution are within the limits of experimental errors and of the errors caused by the approximate character of the system model.

Thus in this paper the fine structure of charge-carrier capture levels connected with the creation of dipole molecule clusters was discovered in the thermoluminescence spectrum of the anthracene crystal with the carbazole dopant. The fulfilled calculation confirms the presented interpretation.

The investigations of model systems give the possibility to determine how and in which clusers dopant molecules are combined in the crystal. In particular, it is shown from Figure 1, that the band corresponding to the pair center with E_a = 0.102 eV is visible even at low concentration of order of 0.3%. Apparently this is connected with the energy gain at formation of such centers, since their total dipole moment is equal to zero (see Figure 3b).

References

1. M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals* (Oxford Univ. Press, London, 1982), 821 p.
2. A. K. Kadashchuk, N. I. Ostapenko, Yu. A. Skryshevskii, V. I. Sugakov and M. T. Shpak, *JETP Lett.*, **46**, 207 (1987).
3. H. Opyrchal, B. Macalik and A. Watterich, *Cryst. Res. Technol.*, **22**, 291 (1987).
4. A. Halperin, A. A. Braner, A. Ben-Zvi and N. Kristianpoler, *Phys. Rev.*, **17**, 416 (1960).
5. B. Basak and B. Lahiri, *Ind. J. Pure. Appl. Phys.*, **7**, 234 (1969).
6. A. V. Tamulis and Sh. P. Kudzmauskas. The investigation of electronic structure of molecules of carbazole, 2,4,7-trinitro-9-fluorenone, 2,4,5,7-tetranitro-9-fluorenone and their single charge ions

by the NDO technique, (Deposited in Lithuanian scientific research institute of scientific and technical information on 11.06.87 n 1908 LI).
7. N. Karl, *Chemia Scripta*, **17**, 201 (1981).
8. O. A. Osipov, V. I. Minkin and A. D. Garnovskii, Handbook on Dipole Moments [in Russian] (Moscow, Vysshaya shkola, 1971).
9. P. Petelenz, U. H. Smith, J. Klein, P. Martin and R. Voltz, *Chem. Phys.*, **112**, 457 (1987).