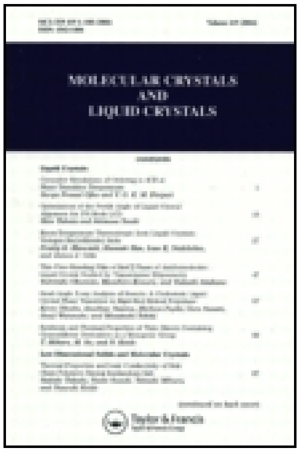

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Charge Carrier Dipole Traps in Neat Molecular Crystals of Polar Molecules

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Charge Carrier Dipole Traps in Neat Molecular Crystals of Polar Molecules.

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The charge-carrier traps in the neat carbazole crystal have been found and were interpreted as dipole traps formed by the intrinsic orientational crystalline defects appearing when a molecule is rotated by 180^0 along the long in-plane axis as compared to the bulk molecules. The depths of trapping states established on the neighboring molecules of crystal in the vicinity of one, two and tree reoriented molecules was calculated. Energetic spectrum of dipole traps was studied by fractional thermoluminescence and the experimental results are in good agreement with calculation.

Keywords: charge-carrier dipole traps, orientational defects, carbazole, thermoluminescence, electrostatic interaction, dipole moment.

INTRODUCTION

The present study is concerned with charge-carrier dipole traps in neat carbazole crystals, which are caused by orientational defects in the crystal of polar molecules. Such crystals often show orientational defects caused by the rotation a molecule by 180^0 along the long in-plane axis as compared to its normal position in the cell [1]. It was suggested [2] that this can lead to the reorientation of the dipole moment of a "defect" molecule, that in turn can originate an additional local electric field of the dipole in the crystal. Electrostatic interaction a charge carrier with this field may establish trapping states in the vicinity of the orientational defect, i.e. dipole traps. The depth both of exciton and charge-carrier traps associated with the above defects have been recently calculated [2], however, up to now there was no experimental evidence of charge trapping by the orientational dipolar defects in the neat molecular crystals.

Experimental and results

Carbazole were purified by means of chemical purification and by zone-refining (>100 zones). Single crystals grown from gas-phase and by the Bridgeman technique, as well as polycrystals grown from the melt were studied. As soon as investigated samples were grown they were immediately used for the thermally stimulated luminescence (TSL) study, which were performed temperature range 4.2-300 K. After UV-light excitation, TSL was measured both at uniform heating with the rate 0.15 K/s and in the fractional heating regime.

Carbazole crystals showed strong TSL which has manifested certain differences depending on crystal growth method and the degree of purification. Fig.1 presents the typical TSL glow curve (curve 1) of freshly prepared carbazole crystal grown from the gas-phase, that provides the most perfect monocrystal samples. TSL glow curve shows a strong low-temperature peak with a maximum at about 65 K and activation energy in the peak maximum equal to 0.15 eV as revealed by the fractional TSL. Intensity of the low-temperature peak at 65 K considerably increases with enhancement of purification of carbazole compound. Curve 2 on Fig.1 presents the TSL glow curve of carbazole crystal of the same purity as given by curve 1, but grown by Bridgeman technique. Such carbazole crystals are characterized by a TSL peak notably shifted towards higher temperatures with a maximum at about 85 K and the activation energy in the peak maximum of 0.25 eV.

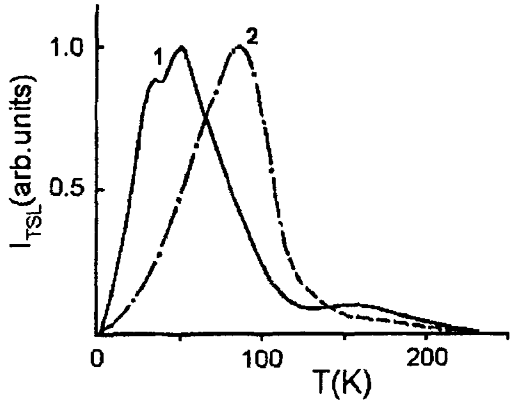

FIGURE 1 Normalized TSL glow curve of carbazole crystals grown from gas-phase (curve 1) and by the Bridgeman technique (curve 2).

We should stress that the intensity of TSL peak of freshly prepared crystals is definitely unstable with time and shows a considerable reduction in the course of the preliminary sample annealing at room temperature.

Calculations and Discussion

We assume that the observed low-temperature TSL peak in carbazole crystal is caused by the charge carrier trap of crystalline structural origin due to the following. (i) The intensity of this peak increases with an enhancement of carbazole purification; (ii) Its intensity is maximal in freshly grown crystals and notably decreases after crystal annealing at room temperature; (iii) The activation energy in the TSL peak depends on the crystal growth method (0.15 and 0.25 eV for crystals grown from the gas-phase and by the Bridgman by the reoriented molecule and is zero for bulk molecules. Several examples of arrangements for charge carrier and reoriented molecules are shown in Fig.2. (A, B, C for one, two, and three defect molecules, respectively).

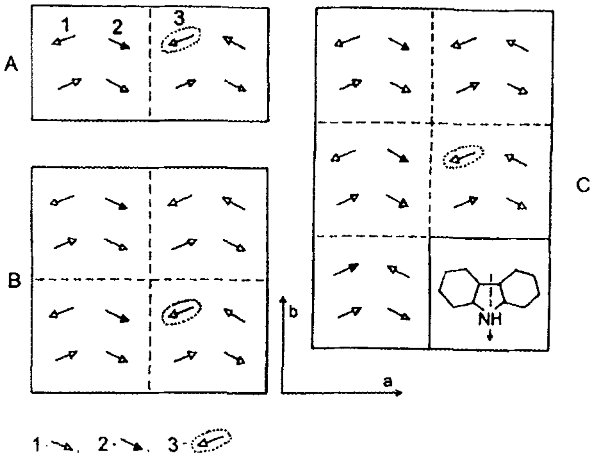

FIGURE 2 Examples of arrangements for charge carrier and reoriented molecules in the case of the deepest levels in ab plane carbazole crystals for one (A), two (B) and three (C) defect molecules respectively: 1 – carbazole molecule, 2 – reoriented carbazole molecule, 3 – ionized carbazole molecule.

The calculations for the various mentioned arrangements have been done. Calculation parameters are $\varepsilon=3$, $|p_\alpha| = 2.1$ D. The results of calculations are presented in Table 1 for the deepest levels. The calculations predict the range of trap depth from 0.01 to 0.28 eV, that is in a good agreement with observed distribution of trap depths.

technique, respectively) that governs the creation of crystalline structural defects and their concentration. Further, we found that the intensity of this peak is near the same for the crystals grown by both methods. However, it is known that concentration of ordinary crystalline structural defects as dislocations in latter case is in several orders higher if compare with crystals grown from the gas-phase. Thus, the structural defects like dislocations probably are not responsible for observed charge traps in carbazole crystals.

We suppose that observed low-temperature TSL peak is due to the presence of orientation defects which create the dipole traps for charge carriers. To justify this assumption we calculate depth of dipole traps in carbazole crystal with orientational defects. The crystal molecule site is defined by the radius vector $\bar{n}_\alpha = n_a \cdot \bar{a} + n_b \cdot \bar{b} + n_c \cdot \bar{c} + \bar{r}_\alpha$, where $\bar{a}$, $\bar{b}$, $\bar{c}$ are the basic vectors of the cell, $\bar{r}_\alpha$ is the radius vector of a molecule α with origin in the cell. For carbazole crystal $\bar{r}_1 = (0,0,0)$, $\bar{r}_2 = (a/2, 3b/2, c/2)$, $\bar{r}_3 = (a/2, b, c/2)$, $\bar{r}_4 = (a, -b/2, c)$ [2]. The narrowness of the conduction band allows us to treat the electron as localized on a crystal site (let's denote this site as $0\alpha_0$.) The presence of orientational defect leads to the shift in the energy of the localized electron in respect to that of the ideal crystal. Supposing that dipole moment of crystal molecule is located in its gravity center, the energy shift for electron can be expressed as:

$$\Delta E_{0\alpha_0} = -\frac{2e}{\varepsilon} \sum_{n\alpha} \frac{\bar{p}_\alpha . \bar{r}_{n\alpha,0\alpha_0}}{|r_{n\alpha,0\alpha_0}|^3} N_{n\alpha} \tag{1}$$

where p_α is dipole moment of molecule α; ε is the dielectric constant; $r_{n\alpha,0\alpha_0}$ is a radius-vector pointing from the reoriented molecule to the site where charge carrier is located; $N_{n\alpha}$ is a value that is unity if the site n_α is occupied

TABLE 1 Calculated depth of dipolar traps caused by reoriented molecules

Trap depth, eV	Position of 1st reorient. molecule				Position of 2nd reorient. molecule				Position of 3rd reorient. molecule			
	n_1	n_2	n_3	α	n_1	n_2	n_3	α	n_1	n_2	n_3	α
-0.17 (*)	-1	0	0	2	-	-	-	-	-	-	-	-
-0.23 (**)	-1	0	0	2	-1	1	0	2	-	-	-	-
-0.27 (***)	-1	0	0	2	-1	1	0	2	-1	-1	0	1

(*), (**), (***) corresponds to single, pair and triple center, respectively.

Since a charge carrier, eventually cascades down to the site allowing the lowest energy, only the deepest levels of calculated ones could be observed in experiment. For instance, the measured trap state with depth of 0.15 eV is close to the calculated value of 0.18 eV (in the case of one rotated molecule). The experimental data for more defect samples reveals additional TSL peak at 85 K. We can conclude that this peak probably originates from more complex centers formed by several rotated molecules. Actually, the experimental value of 0.25 eV is pretty close to calculated depth of the deepest levels which correspond to the clusters consisting of two and three reoriented molecules (0.23 and 0.27 eV, respectively). Thus, an increase of defect concentration enhances the probability of appearing more complex trapping centers.

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