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## Molecular Crystals and Liquid Crystals

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### Trapping States Formed by Structural Defects in Molecular Crystals

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# Trapping States Formed by Structural Defects in Molecular Crystals

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**Abstract**—Results of calculations of the energetic distributions of trapping states in simple molecular crystals are given in the paper. A crystal with primitive regular unit cells has been taken into account, and three kinds of simple isolated linear defects have been considered: an edge dislocation, a linear array of vacancies, and a defect formed by a linear array of molecules larger than the host ones. Equilibrium positions of molecules in the vicinity of the defects have been calculated describing the intermolecular interactions by the Lennard-Jones type potential function. Local values of the polarization energy and hence depths and distributions of traps formed by molecules neighbouring to the defects have been calculated in the ion-dipole approximation. It has been shown that the formation of trapping states by thermal vibrations can be neglected as being a small effect.

## 1. Introduction

In the previous paper<sup>(1)</sup> a qualitative description was presented explaining the origin of trapping states in molecular crystals. It was shown that a molecule in the crystal can act as a trap if the local value of the energy of electrostatic interactions between a carrier localized on the molecule and surrounding neutral molecules (polarization energy) differs from that of other molecules.† The local changes of the polarization energy can be due to changes of intermolecular distances resulting from the presence of structural defects in the crystal.

Trapping states attributed to structural defects in molecular crystals have been experimentally found in several materials, their

† In this paper the term "local value of the polarization energy" will be used. It is a simplification used to denote the value of the polarization energy of the crystal lattice due to the presence of a current carrier on the molecule considered.

energetic distribution often being described in a wide range of energies by the exponential distribution function

$$h(E) = \frac{H}{kT_c} \exp\left(\frac{E}{kT_c}\right), \quad (1)$$

where  $E$  is the trap depth ( $E \leq 0$ ),  $H$  is the total density of traps, and  $kT_c$  is the characteristic energy of the trap distribution.

The review of experimental data shows that both the chemical nature of molecules forming the crystal and the crystal symmetry weakly influence the trap distribution; in other words, similar distributions of trapping states have been observed, for example, in triclinic tetracene, monoclinic anthracene and phthalocyanine, and orthorombic sulphur and iodine. It seems therefore to be justified to consider as a model a crystal with primitive regular unit cells consisting of globular molecules. Let us introduce into the lattice a single isolated defect. Three types of defects will be considered: an edge dislocation, a linear array of vacancies, and—for comparison—a linear array of larger molecules.† For the sake of definiteness we will consider the defects directed along the  $[001]$  direction. In the subsequent calculations the lattice constant will be equal to  $6 \text{ \AA}$  and the molecular polarizability will amount to  $2.5 \times 10^{-23} \text{ cm}^3$ .

## 2. Deformation of the Crystal Lattice Near the Defect

In order to find the equilibrium positions of molecules near a defect one must find conditions for the minimum of the potential energy for each molecule in the crystal. In other words, for each molecule a set of equations should be solved

$$\sum_i \frac{dU}{dr_j^i} = 0, \quad (2)$$

where  $U$  is the potential energy of intermolecular interactions, and  $r_j^i$  is a component of the distance between the considered molecule and an  $i$ th one along a  $j$ th principal direction ( $j = 1, 2, 3$ ). The

† The “linear array of larger molecules” is a model linear defect consisting of the linear array of molecules having larger dimensions than the host ones but the other physical properties being the same.

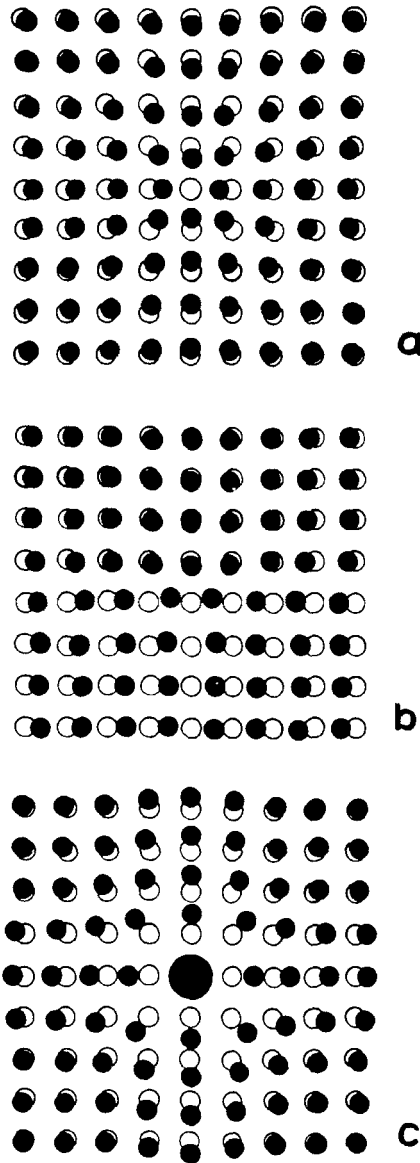


Figure 1. Equilibrium positions of molecules in the planes perpendicular to the linear array of vacancies (a), the edge dislocation (b) and the linear array of larger molecules (c). The positions of molecules in the perfect lattice are marked by open circles.

potential energy is assumed to be described by the Lennard-Jones type function

$$U_i = -Ar_i^{-6} + Br_i^{-12}, \quad (3)$$

the constants  $A$  and  $B$  being related through the equation

$$A = 2\gamma Br_0^{-6}, \quad (4)$$

where  $r_0$  is the lattice period and  $\gamma$  is a constant depending on a crystal lattice. In the regular primitive lattice

$$\gamma = \frac{\sum_{m,n,p} (m^2 + n^2 + p^2)^{-13/2}}{\sum_{m,n,p} (m^2 + n^2 + p^2)^{-7/2}}, \quad (4a)$$

( $m, n, p$  are integers, the point  $m = n = p = 0$  being excluded). Inserting Eq. (4) into (2) one obtains equations which may be solved by numerical methods only. Hence a position of each molecule can be calculated, and this procedure has to be repeated for all molecules surrounding the defect a number of times (up to 70) to attain self-consistency. The calculations reported here have been performed for 134 molecules nearest to the edge dislocation in the (001) plane, and for 360 molecules in the two other cases. The equilibrium arrangements of molecules in the (001) planes nearest to the three considered defects are shown in Fig. 1.

### 3. Calculation of the Trap Distribution

As has been already mentioned, local values of the polarization energy depend on changes of intermolecular distances in the vicinity of defects; it is therefore possible to calculate the depths and the energetic distributions of traps formed in this way.

One may expect that a molecule can act as a trap if the local value of the polarization energy is greater than the polarization energy in the crystal far away from the defect.† In the calculations reported

† This condition is strictly true when the free path of a carrier is greater than the dimensions of a defect. If the opposite situation takes place (the carrier pathway in a crystal is then comparable with the lattice spacing), the depth should be equal to the difference between energies of final and initial sites on which an electron would be localized.

here the polarization energy was approximated by the ion-dipole term only

$$P = \sum_i \frac{e^2 \alpha}{2r_i^4} \quad (5)$$

where  $e$  is the unit charge and  $\alpha$  is the molecular polarizability. The summation has been performed over 124 molecules next-nearest to the molecule on which a current carrier had been localized. Neglecting farther molecules in the summation procedure leads to an error of the order of a few per cent (cf. Ref. 6). A relatively great error may be introduced because of neglecting higher terms in the polarization energy; however, since the ion-dipole term dominates all other ones, this error is believed not to influence strongly the trap distribution.

Local values of the polarization energy and hence trap depths have been calculated. The results of those calculations are shown in Fig. 2 in the form of histograms where the energetic distributions have been plotted for the three kinds of defects discussed above.

It is noteworthy to indicate that the total density of traps available for carriers is lower than the number of molecules with local values of the polarization energy greater than the mean value because of coulombic forces acting between trapped and free carriers. Let us consider the following simple model: a first carrier moving to a disturbed region of a crystal should be trapped and — because of electrostatic interactions — any other carrier must not be trapped at a distance smaller than a coulomb radius ( $R_c$ ). As a rule, the coulomb radius in molecular crystals is of the order of several tens of angstroms, i.e. it should be greater than dimensions of structural defects, thus the other carrier can be trapped by a site around another defect. Since there is no correlation between the coulomb radius and a distance between defects, one may assume that carriers are localized randomly in trapping sites in the solid, and in consequence only the trap density is reduced by some factor, the energetic distribution being unaltered. The maximal density of traps which may be filled with carriers can be estimated as

$$H_{\max} \approx (R_c)^{-3} = \left( \frac{\epsilon k T}{e^2} \right)^3 \quad (6)$$

( $\epsilon$  is the dielectric constant), and for typical molecular crystals at

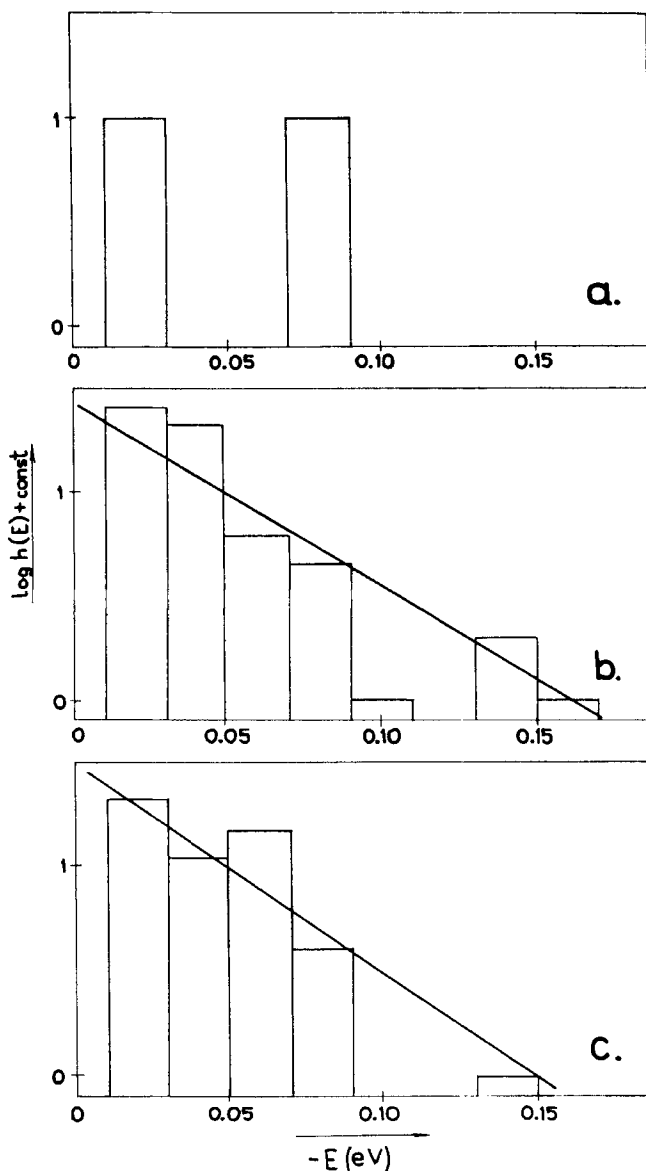


Figure 2. Energetic distributions of structural traps calculated for the linear array of vacancies (a), the edge dislocation (b) and the linear array of larger molecules (c). The straight lines show the exponential distributions of traps according to Eq. (1). Molecules with the local values of the polarization energy lower than the mean value as well as the shallowest traps ( $|E| < 0.01$  eV) are neglected.



room temperatures it is of the order of  $10^{17} \text{ cm}^{-3}$ , being in a good agreement with typical experimental results.

It can be expected that a correlation between the density of structural defects and the density of traps should be observed. Such a correlation has been reported by Thomas and Williams.<sup>(7)</sup> However, one must emphasize that when the distances between neighbouring defects become smaller than  $R_c$ , the trap density should no longer be a function of the number of defects.

#### 4. Effect of Lattice Vibrations on the Trap Distribution

So far the crystal lattice has been considered as a rigid one, and in the calculations reported above the lattice relaxation due to electrostatic interactions and thermal vibrations have been neglected. The former effect will be discussed elsewhere,<sup>(2)</sup> the latter one will be analysed here in detail.

Recently Silinsh<sup>(3)</sup> published a paper where the possibility of the formation of trapping states by thermal vibrations has been discussed. According to the author, traps can be formed by molecules which undergo quasi-static displacements with respect to their neighbours due to the so-called "frozen fluctuations" (the vibration period of which is greater than the trapping time). The amplitude of the frozen vibrations as calculated by Silinsh seems to be overestimated because of the use of an uncorrect Debye temperature for acoustic vibrations in his calculations. In this section of the paper the effect of thermal vibrations on the trap depth and distribution will be re-evaluated.

It is convenient to keep after Silinsh the concept of frozen vibrations, their period ( $\tau$ ) being determined by the inequalities

$$\tau_i \ll \tau < \tau_{\max}. \quad (7)$$

Here  $\tau_{\max}$  is a maximum wave period depending on sample dimensions and  $\tau_i$  is the trapping time

$$\begin{aligned} \tau_{\max} &= \frac{\lambda_{\max}}{v} = \frac{2d}{v}, \\ \tau_i &= \frac{1}{\nu_0} \exp\left(-\frac{E}{kT}\right), \end{aligned} \quad (8)$$

where  $d$  stands for a linear dimension of the crystal,  $v$  is the wave velocity,  $\nu_0$  is a constant being of the order of  $10^{10} \text{ sec}^{-1}$  (Ref. 4), and  $E$  is the trap depth. Since allowed frequencies must not exceed  $\nu_0$ , only long wave acoustic vibrations (with the wave vector  $q \rightarrow 0$ ) should be taken into account. The wave velocity is therefore equal to the sound velocity, i.e. it is of the order of  $10^5 \text{ cm/sec}$ . Such a wave can be considered as a flat one.

The amplitude of acoustic vibrations (measured with respect to an external zero point) at temperatures high enough is given by the equation

$$Z^2 = \frac{kT}{4\pi^2 m \nu^2}, \quad (9)$$

where  $m$  is the molecular mass, and  $\nu$  is the vibration frequency. In the present discussion, however, it is necessary to know a "relative" amplitude (i.e. the amplitude of the position changes of a molecule measured with respect to a neighbouring one). It can be derived from the wave equation

$$y_i = z \exp [i(q\rho_i - 2\pi\nu t)]. \quad (10)$$

Here  $y_i$  stands for the displacement of an  $i$ th molecule from its equilibrium position and  $\rho_i$  is its position vector. Taking into account nearest-neighbouring molecules only and putting  $\rho_0 = 0$  and  $|\rho_{\pm 1}| = r_0 = \text{lattice constant}$ , one obtains for  $qr_0 \rightarrow 0$

$$\Delta y = y_0 - y_{\pm 1} = \frac{1}{2} q^2 r_0^2 \exp(-2\pi i \nu t) = w \exp(-2\pi i \nu t), \quad (11)$$

$w$  being the "relative" amplitude. Inserting it into Eq. (9) one obtains

$$w = \frac{\pi r_0^2 (kT)^{1/2} \nu}{m^{1/2} \nu^2}. \quad (12)$$

Taking  $r_0 = 6 \text{ \AA}$ ,  $T = 300^\circ \text{K}$ ,  $\nu = \nu_0$ ,  $m = 2 \times 10^{-22} \text{ g}$  and  $v = 10^5 \text{ cm/sec}$  as typical values one obtains  $w$  equal to  $2 \times 10^{-2} \text{ \AA}$  approximately, i.e. the quotient  $w/r_0$  does not exceed  $10^{-2}$ .

Now, let us estimate the depth of the deepest traps possible to be formed by the lattice vibrations. As it has been indicated before, the trap depth can be calculated as a change of the polarization energy due to changes of intermolecular distances ( $\Delta r_i$ ). For small  $\Delta r_i$  one may write

$$E = -\Delta P = -\sum_i \frac{\partial P}{\partial r_i} \Delta r_i = 2e^2 \alpha \sum_i \frac{\Delta r_i}{r_i^5}. \quad (13)$$

Taking into account the interactions between nearest neighbours only and assuming the acoustic wave to be flat the following relationship can be derived (valid only for small "relative" amplitudes  $w/r_0 < 0.1$ )

$$E_{\max} = -\frac{5.5e^2\alpha w}{r_0^5}. \quad (13a)$$

Assuming  $\alpha = 25 \text{ \AA}^3$  one obtains  $E_{\max} = -4 \times 10^{-3} \text{ eV}$  approximately which is less than  $kT$ . Therefore it has been proved that the effect of thermal vibrations is insignificant and can be neglected.

## 5. Conclusions

The results of the calculations presented here seem to confirm the model of trap formation proposed in the previous paper.<sup>(1)</sup> It must be stated, however, that a fully quantitative agreement with experimental data has not been reached. There may be several reasons explaining this fact, the first of them being the approximation assuming the crystal as a rigid body. As has been shown in the preceding section, lattice vibrations can be neglected here; however, the lattice deformation due to the localization of a carrier on a molecule, neglected in the present calculations, can introduce a serious error. The influence of the latter process will be discussed elsewhere.<sup>(2)</sup>

The calculations have been performed for three simple isolated defects. Any interactions between the defects as well as the presence of other types of defects have been neglected. Moreover, the anisotropy of both molecular properties and intermolecular interactions has not been taken into considerations. Simultaneous occurrence of several different types of defects should lead to an energetic distribution of traps which could be described by a Gaussian function, as has been proposed by Silinsh.<sup>(3)</sup>

All the factors mentioned above, when taken into account, should improve the consistency of the model. In the author's opinion, however, it seems possible that at least two types of trapping states co-exist in organic solids. The shallower traps may be formed by structural defects, whereas the deeper ones could be due to undefined impurities present in crystals in very small (even undetectable) concentrations. There are not many experimental data supporting

this hypothesis; the results obtained by Schadt and Williams<sup>(5)</sup> on pure anthracene crystals are believed to be in agreement with the author's view.

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