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Structural Disorder as a Source of Traps in Organic Crystals

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Structural Disorder as a Source of Traps in Organic Crystals

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In 1970, a simple model was put forward[1] attempting to explain the appearance of traps, and based on the assumption that traps for current carriers may be formed on chemical and structural defects because of local changes of the polarization energy. The predictions were then followed by numerical computations carried out on a simple model lattice, and by preliminary calculations of traps in anthracene performed using the atom–atom potentials.[2]

The aim of this communication is to present results of computations carried out for a model crystal consisting of anisotropic molecules and to discuss a possibility of formation of deep traps by structural defects.

THE ARRANGEMENT OF MOLECULES IN A PERFECT MODEL CRYSTAL

It has been demonstrated[2] that the atom-atom potentials scheme[3] may be employed to calculate the arrangement of molecules near a given defect. However, as most of symmetry relations must be broken in this case, the computations require a lot of computer time, unless simplifications either in computations themselves or in the model are introduced. Fortunately, for a qualitative discussion it is not necessary to carry out the computations on a real crystal, and some conclusions can be drawn on the basis of results obtained for a crystal built of model anisotropic molecules. It has been assumed that the molecules consist of six spherical elements (corresponding to some extent to atoms in the Kitaigorodskii's model) placed inside an ellipsoid. For each sphere, a simple isotropic 6–12 potential has been adapted.

As a first step, a structure of a perfect crystal has been calculated assuming the space group $P2_1/a$. The unit cell parameters obtained from the calculations are: $a = 11.44$ Å, $b = 3.30$ Å, $c = 9.42$ Å, $\beta = 92°42'$. The arrangement of molecules is shown in Figure 1.

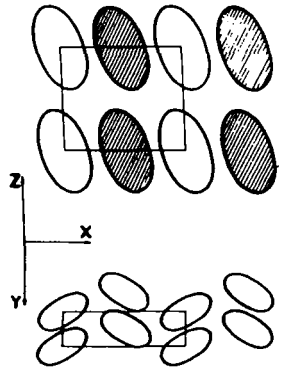

FIGURE 1 The arrangement of molecules in the (010) and (001) planes of a perfect crystal.

ARRANGEMENT OF MOLECULES NEAR A DEFECT

Relatively low values of the lattice energy (of the order of 10–100 kJ/mole) suggest that the formation of point defects is relatively easy (see, for example Ref. 4 and references quoted therein); there is also a number of extended defects present in those materials.

An attempt has been made to calculate the positions of molecules surrounding a point defect shown in Figure 2. The introduction of the defect leads to some changes in the arrangement of molecules, and in consequence traps for current carriers may arise, similarly as in the case of other structural defects.

The interaction potential identical to that employed previously to the perfect crystal has been used to find the positions of molecules in the defected crystal. The resulting molecular arrangement is shown in Figure 2.

DEPTHS OF TRAPS

According to the model which has been put forward in Ref. 1, traps may occur as a result of local changes of the polarization energy, i.e. the energy of

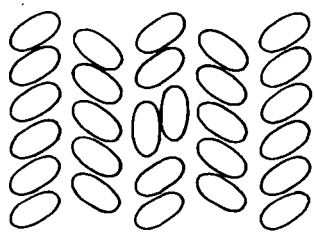

FIGURE 2 The arrangement of molecules surrounding the defect discussed in the text.

electrostatic interactions between an ion and surrounding polarizable neutral molecules. Suitable calculations of the polarization energy were performed using the equations proposed by Lyons and collaborators[5]

$$P = P_{id} + P_{dd}$$

where

$$P_{id} = -\sum_i \frac{e^2}{2r_i^6} (r_i)^T (m_i)(B)(m_i)^T (r_i)$$

and

$$P_{dd} = G^2 e^2 \sum_{i>j} r_i^{-3} r_j^{-3} r_{ij}^{-3} \{(r_i)^T (r_j) - 3r_{ij}^{-2} [(r_i)^T (r_{ij})][(r_j)^T (r_{ij})]\}$$

In the above equations (r_i) and (r_j) are column matrices representing distances of ith and jth molecules from the ion, (m_i) is the direction cosines matrix, (B) is the polarizability matrix, and G is the average polarizability of the molecule.

The polarization energy calculated for the perfect crystal amounted to 2.59 eV, and the maximal trap depth associated with the defect shown in the preceding section was 0.28 eV. The value seems to be be typical for traps associated with the presence of structural defects. Formation of deeper traps of the polarizational origin would require a substantial local contraction of the crystal lattice. To give an estimation of the probability of the occurrence of such defects, semi-quantitative calculations of forces necessary to induce uniaxial contractions were carried out. The results obtained seem to indicate that one should not expect any defects involving local contractions greater than ca. 3–10%. Extrapolating the results given by Silinsh *et al.*[6] one should expect an increase of the polarization energy of the order of ca. 0.2 to 0.5 eV. Therefore, one may conclude that the occurrence of traps of the polarizational origin deeper than ca. 0.5 to 0.6 eV should be rather impossible, and traps ca. 1 eV deep commonly observed in various experiments are probably associated with chemical impurities.

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