Calculation of trap depths for a charge carrier around the (010)(001) dislocations in anthracene crystals

LETTER TO THE EDITOR

Calculation of trap depths for a charge carrier around the [010](001) dislocations in anthracene crystals

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Abstract. Changes of the polarization energy of a crystal by an excess charge carrier due to the presence of the [010](001) edge or screw dislocations in anthracene crystals have been calculated. The maximum changes (trap depths) have been found to be -0.14 eV at the compressive region around the edge dislocation. It was revealed that the strong anisotropy of polarizability of an anthracene molecule led to trap depths of -0.11 eV (comparable to those of the edge dislocation) around the screw dislocation having no compressive strains but only shear strains. One-dimensional arrays of traps and anti-traps appeared alternately around the screw dislocation.

Trapping phenomena of current carriers in organic molecular crystals have been commonly observed in experiments (Silinsh 1980, 1990). Silinsh (1970) and Sworakowski (1970, 1976) suggesting that any structural disorder would give rise to the appearance of traps because of local changes in the polarization energy. Mokichev and Pakhomov (1982) studied equilibrium configurations for the core of a [010](001) edge dislocation in a naphthalene crystal and then calculated the trap depths around the dislocation. Their model used to obtain the relaxed configurations consisted of 72 molecules. They obtained a broad spectrum of trapping and anti-trapping levels (-0.1 to $+0.19$ eV). Munn and co-workers developed the Fourier transform method and investigated local states in the vicinity of lattice vacancies using unrelaxed lattices (Eisenstein *et al* 1983, Eisenstein and Munn 1983).

In this letter we report the calculation of trap depths for an excess charge carrier around [010](001) edge and screw dislocations in anthracene crystals. In estimating the polarization energy, we used molecular configurations obtained by Ide *et al* (1990, 1991), where the relaxation radius was taken to be $16b$ (1062 and 758 molecules), where b is the magnitude of the Burgers vector. The edge dislocation had a spread-out shear misfit, and its width of Burgers vector density at half-peak height reached $6.2b$. The screw dislocation had a compact core region, but the molecular configurations were strongly anisotropic.

The charge carrier residence time on a lattice site in anthracene crystals is greater than the relaxation time for the electronic polarization of surrounding molecules (Silinsh 1980). Therefore the crystal polarization energy can be estimated through a microscopic electrostatic theory, and the polarization by a quasi-localized charge carrier determines its self-energy and the position of the carrier's conduction level.

Structural imperfections in the crystals change the polarization energy and causes the presence of a local level. Then a carrier trap depth ΔP is given by

$$\Delta P_m = P_m^{\text{def}} - P^{\text{perf}} \tag{1}$$

where P_m^{def} is the polarization energy of a crystal having a defect with a carrier at site m, P^{perf} is that of a perfect crystal polarized by a carrier.

In the present work the self-consistent polarization field (SCPF) method (Druger and Knox 1969, Jurgis and Silinsh 1972) has been used. The essence of the SCPF method consists of considering every induced dipole as being in the field of the localized charge carrier and in the self-consistent field of other induced dipoles, and the polarization energy P of the localized charge carrier can be calculated by means of the following expression

$$P = -\sum_i \left(E_0(r_i) \cdot \mu_i + \frac{1}{2}\mu_i T_i^{-1} \alpha^{-1} T_i \mu_i - \sum_{j>i} \mu_i \Lambda_{ij} \mu_i \right) \tag{2}$$

where $E_0(r_i)$ is the electric field at a molecule i due to a localized carrier, μ_i and μ_j are the values of induced dipole moments on molecules i and j, respectively, T_i is a transformation matrix from the molecular principal axis to the crystal axis, α is the polarizability tensor of the molecule and Λ_{ij} is the tensor of dipole–dipole interaction

$$\Lambda_{ij}^{kl} \equiv [(r_{ij})^2 \delta_{kl} - 3r_{ij}^k r_{ij}^l]/(r_{ij})^5 \tag{3}$$

r_{ij} being the distance between the dipoles. The second term of equation (2) describes the self-energy of the induced dipole μ_i. The dipole moments were determined from the expressions that were derived from equations $\partial P/\partial \mu_i^k = 0$. A Gaussian elimination method was adopted in this evaluation because the iteration method used by other authors (Jurgis and Silinsh 1972) did not give a convergent solution.

The polarization energy P was calculated for a sphere of radius of 3.5 nm for the edge dislocation and for that of 4.0 nm for the screw dislocation: these spheres, with their centres at charge carriers, contain 804 molecules and 1182 molecules respectively. It was deduced from several runs with increasing radii that these restrictions on radii would give errors within about 0.01 eV. The following values of the polarizability tensor components for the anthracene molecule (Le Fevre 1963) were used: $\alpha_L = 3.39 \times 10^{-2}$ nm^3, $\alpha_M = 2.92 \times 10^{-2}$ nm^3 and $\alpha_N = 1.29 \times 10^{-2}$ nm^3, where L, M and N represent the three symmetry axes of the molecule. A perfect crystal of anthracene with monoclinic symmetry (space group $P2_1/a$) has two non-equivalent molecules, one at the corner of a unit lattice (hereinafter referred to as a corner molecule), and the other at the centre (a centre molecule).

Figure 1 shows the positions of molecules around the edge dislocation and the values of ΔP with the excess charge localized at the molecules. In the compressive region above the glide plane, traps are formed with a broad spectrum, and anti-traps are formed under that plane. There is some approximate symmetry of distribution of the traps and anti-traps with respect to the extra half plane. The maximum trap depths are -0.14 eV, being at two sites located about $2b$ away from the extra half plane. This splitting occurs for the following reasons. First, the edge dislocation has a spread-out (about $5b$) shear misfit along the slip plane, and moreover, compressive
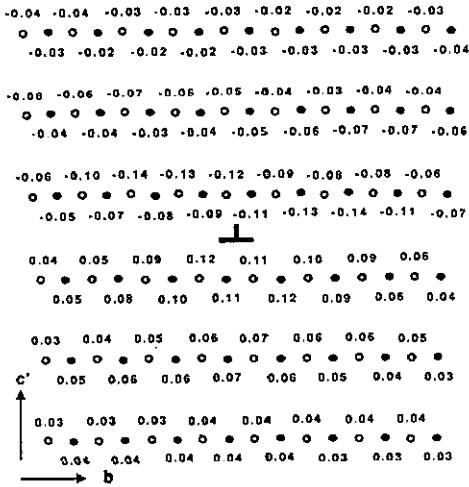
-0.04 -0.04 -0.03 -0.03 -0.03 -0.02 -0.02 -0.02 -0.03
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  -0.03 -0.02 -0.02 -0.02 -0.03 -0.03 -0.03 -0.03 -0.04

-0.08 -0.06 -0.07 -0.06 -0.05 -0.04 -0.03 -0.04 -0.04
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  -0.04 -0.04 -0.03 -0.04 -0.05 -0.06 -0.07 -0.07 -0.06

-0.06 -0.10 -0.14 -0.13 -0.12 -0.09 -0.08 -0.08 -0.06
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                         ⊥

 0.04   0.05   0.09   0.12   0.11   0.10   0.09   0.06
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   0.05   0.08   0.10   0.11   0.12   0.09   0.06   0.04

 0.03   0.04   0.05   0.06   0.07   0.06   0.06   0.05
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↑
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│ o ● o ● o ● o ● o ● o ● o ●
│   0.04   0.04   0.04   0.04   0.04   0.03   0.03   0.03
└───→ b

Figure 1. Influence of the edge dislocation on the polarization energy of a crystal by a carrier localized each molecule; solid circles and open circles denote the positions of corner and centre molecules near the edge dislocation, respectively; the number beside the molecules gives ΔP in eV.

 0.01 -0.01 -0.02 -0.01 -0.02 -0.02 -0.03
 ● o ● o ● o ● o ● o ● o
   0.00   0.01   0.02   0.03   0.03   0.02   0.01

-0.01 -0.01 -0.02 -0.03 -0.03 -0.04 -0.03
 ● o ● o ● o ● o ● o ● o
   0.00   0.02   0.03   0.04   0.02   0.01   0.00

 0.00 -0.01 -0.01 -0.05 -0.11 -0.06 -0.03
 ● o ● o ● o ● o ● o ● o
   0.01   0.03   0.05   0.02   0.00   0.00   0.00

 0.00   0.00   0.00   0.02 Ⓢ 0.06   0.03   0.01
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 0.00   0.01   0.02   0.04   0.03   0.02   0.00 │
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                                            ──→ a
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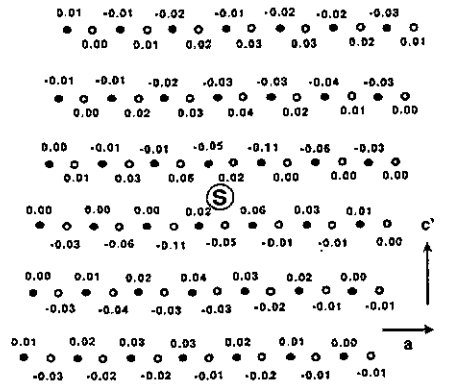 -0.03 -0.02 -0.02 -0.01 -0.02 -0.01 -0.01

Figure 2. Influence of the screw dislocation on the polarization energy of a crystal by a carrier; solid circles and open circles denote the positions of corner and centre molecules near the screw dislocation respectively; the number beside the molecules gives ΔP in eV. The dislocation line runs through the position **S**.

strains at those sites are a little larger than at the extra half plane. Second, the shear strain along the dislocation line is relatively large at those sites (see figure 5 of the paper by Ide *et al* (1990)) and it raises the polarization energies of centre molecules and reduces those of corner ones or *vice versa* as will be explained later.

Calculated values of ΔP around the screw dislocation are presented in figure 2. It should be noted that one-dimensional arrays of traps and anti-traps appeared alternately along the basal planes around the screw dislocation, and that the maximum trap depths reach -0.11 eV, comparable to those of the edge dislocation. These are caused by the strongly anisotropic polarizability of the anthracene molecule as follows. Figure 3 shows schematically the positions of molecules on the (001) plane of the perfect crystal (a) and those of the crystal possessing a shear strain (b). When molecules are displaced due to the screw dislocation like (b), the b and c molecules move nearer to the e molecule, and the a and d molecules move away from it. If a carrier localizes at the e molecule, the polarizabilities of the b and c molecules are small (about 1.8×10^{-2} nm^3), and those of the a and d molecules are large (about 2.8×10^{-2} nm^3). Then the polarization energy of this strained crystal becomes smaller than that of the perfect crystal. However, if a carrier localizes at the d molecule, the polarization energy becomes larger than that of the perfect crystal.
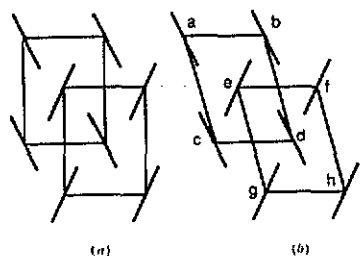
Figure 3. (*a*) Schematic diagram of the positions of molecules on the (001) plane of the perfect crystal and (*b*) that of the crystal possessing shear strain. The shear displacements of the screw dislocation alter the molecular positions like (*b*).

Maeta and Sakaguchi (1979) have used computer-simulated analysis of the thermally stimulated current spectra obtained for anthracene single crystals. They have detected ten closely spaced shallow trapping levels in the 0.03 to 0.34 eV energy interval which form a wide overlapping band, as well as two distinct deeper levels at 0.51 and 0.60 eV. Our calculations of the trap depths indicate that the traps around the dislocation line or the dislocation alignments can be the origins of these shallow levels as well as traps around the vacancies.

We conclude that the charge traps around the dislocation are induced by the two mechanisms. One is due to decrease in inter-molecular distance, which appears in compressive sites as in the case of the edge dislocation. The other is due to the strongly anisotropic polarizability of the anthracene molecule itself, appearing in sheared sites in the case of the screw dislocation.

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