Polymorphism and electronic properties of pentacene
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Chapter 5

Electronic structure and charge transport properties

5.1 Introduction

Pentacene thin films have been studied extensively during the last decade. With improving sample preparation, the observed mobility became increasingly higher, which made it a promising candidate for electronic devices. The temperature dependence of the mobility varied highly and various models have been proposed to describe the different types of behaviour. A field effect transistor is a tool to measure the charge transport through thin films. The electrostatically injected charge allows us to measure a current through the thin film.

Recently Schön, Kloc, and Batlogg (SKB) have performed space-charge-limited-current measurements on organic molecular crystals. Using ultra pure single crystals they could reach the trap-filling limit, above which a mobility could be measured that was not hindered by grain boundaries and impurities. The observed charge transport behaviour was, at low temperatures, described as band like transport, which crosses over, at higher temperatures, to a hopping mechanism [1,2]. This measurement technique gives, apart from the mobility, also information about the number of traps and their activation energy.

Generally, there are two methods to measure the mobility in these materials: time of flight and current-voltage characteristics. We have studied
the charge transport properties of polycrystalline pentacene thin films using
the current-voltage characteristics of thin film transistors. Our single crys-
tals have also been studied by current-voltage characteristics. High electric
fields were applied, and space-charge-limited-current (SCLC) behaviour was
observed. In this chapter we will discuss our experimental results.

From SCLC measurements SKB [1] determined a marked anisotropy in
the pentacene ab plane. We present band structure calculations for one layer
of pentacene molecules, as well as for single crystalline pentacene. A tight-
binding fit is performed on the band structure and the effective mass is calcu-
lated for the different crystallographic directions. The observed anisotropy
in the effective mass is compared to the results of SKB. From the difference
in anisotropy we make an estimate of the effect of the dispersion interactions
in pentacene.

5.2 Thin film transistors

5.2.1 Device preparation

Our thin film transistors (TFTs) were prepared as follows. Highly doped
silicon was used as gate electrode. The top layer of these silicon wafers was
thermally oxidized and formed a 1 \( \mu m \) thick insulating layer. The contact
electrodes were made by e-beam evaporation under a vacuum of \( 10^{-7} \) mbar
through a shadow mask onto the \( \text{SiO}_2 \). They consisted of stripes of 5 nm
titanium and 40 nm gold. The distance between the contact electrodes was
125 \( \mu m \). The organic layer was applied by high vacuum evaporation as
described in chapter 2. Around the contacts the pentacene was carefully
scratched away to insulate the different devices from each other. The \( d(001) \)
value of the crystal structure of the deposited organic layer was measured using X-ray diffraction. A schematic picture of this device can be seen on the left side of figure 5.1.

However, depending on the kind of the experiment and the form of the material, other device geometries are possible. Constructing a FET with a single crystal as active layer cannot be done in the way described above. To form a well-defined interface between the insulator and the crystal, the oxide should be deposited on top of the crystal, see the right side of figure 5.1.

An important requirement for good performance of a FET is a high quality insulator. If the conduction through the oxide becomes in the same order of magnitude as the channel conduction, the device will not work properly, the current will start to flow through the oxide to the gate, instead of from source to drain. The leakage current through the $\alpha$-SiO$_2$ of our TFTs was typically 0.5 nA/mm$^2$.

Layers of Al$_2$O$_3$ were rf-sputtered (2 kV, 220 mA) using a Leybold-Heraeus Z400, with 3 · 10$^{-5}$ mbar O$_2$ and Ar in the chamber. These layers, approximately 100 nm thick, resulted in FETs with a leakage current of 20 nA/mm$^2$ with an applied voltage of 40 V. Using a higher oxygen pressure gave slightly better results, but the oxide did not become of such quality that it could be used in the FET configuration.

A possible solution is to make a thicker oxide layer. But this influences the capacitance of the insulator, $C_{ox} \sim d^{-1}$ and therefore the number of injected charge carriers, $C_{ox} = neV_g^{-1}$. In order to inject the same number of carriers in a FET with a thicker oxide layer, a higher gate voltage should be applied.
In the case of a "normal" transistor, operated in a voltage regime up to 40 V, this is a possibility. To observe superconductivity induced by charge injection [4–6] a very high quality oxide layer is prerequisite. This type of experiments requires the injection of stoichiometric amounts of carriers. To accomplish this for pentacene, we would have to inject 2 electrons per unit cell area (ab plane). If we could manage to produce a good insulating layer of 20 nm thick, with a capacitance of 170 nF/cm², we would have to apply a gate voltage of ~ 350 V to inject this amount of charge. But such a high voltage is near the breakdown voltage for a thin oxide layer of 20 nm.

5.2.2 Measurements and analysis

Measurements were performed in a home build probe station, which could be cooled down to liquid nitrogen temperature. Devices were held in darkness and in a vacuum of 1 · 10⁻⁶ mbar. I-V characteristics were measured using an HP4155B Semiconductor Parameter Analyzer.

In figure 5.2 a typical example of a I-V characteristic of a pentacene thin film transistor is shown. These curves were measured on a TFT with the 15.4 Å polymorph of pentacene as active organic layer. The pentacene was deposited on α-SiO₂ by vacuum sublimation at room temperature.

With increasing negative gate bias the number of positive charge carriers in the channel accumulates, resulting in larger currents. If the gate voltage goes towards negative values, the current becomes lower, until the layer is depleted of free carriers and negative charge carriers are induced in the conduction channel. The boundary between the accumulation and the inversion mode is called the threshold voltage. Inversion was not observed in our TFTs of pentacene. The limitation of the conduction to one type of carriers is generally ascribed to trapping of the electrons [7,8].

For small drain voltages the TFT is said to be operated in the linear regime. If the drain voltage is increased the gate field is no longer uniform and a depletion area is formed at the drain contact. Beyond this source-drain voltage the current becomes saturated.

In the standard description of the I-V characteristics of a MOSFET the mobility is either calculated from the linear or the saturation regime [3]. Because of the uniform charge distribution in the channel, the charge transport properties are preferably determined from the linear regime [9]. Therefore,
the drain current was measured as function of the gate voltage for various small source-drain voltages, see figure 5.3.

The current between the source and drain contact in the linear regime of operation of the TFT is given by:

\[ I_{sd} = \frac{Z}{L} \mu C_i (V_g - V_t) \cdot (V_{sd} - V_{\text{contact}}) \]  

(5.1)

with \( I_{sd} \) the source-drain current, \( Z \) and \( L \) the channel width and length respectively, \( \mu \) the charge carrier mobility, \( C_i \) the capacitance of the insulating layer, \( V_g \) the applied gate voltage, \( V_t \) the threshold voltage, \( V_{sd} \) the applied source-drain voltage and \( V_{\text{contact}} \) a correction factor for the contact resistance. In this case this value is small, 0.4 V.

In figure 5.3 the source-drain current is shown as function of the applied gate voltage. Indeed, the channel current increases linearly with the gate

![Diagram](image_url)

**Figure 5.2:** Typical example of an I-V characteristic of a pentacene thin film transistor. Source-drain current as function of source-drain voltage for different values of the gate bias.
Figure 5.3.: Typical example of an I-V characteristic of a pentacene thin film transistor. The source-drain current is shown as function of gate voltage, for different values of the source-drain voltage. The inset shows the current as function of drain voltage at a constant gate voltage. From this graph the correction factor for the contact resistance, $V_{\text{contact}}$, was calculated to be 0.4 V.

voltage, therefore the channel conductance, $g_c$ can be determined from this curve [3]:

$$g_c = \frac{\partial I_{sd}}{\partial V_{sd} V_g} = \frac{Z}{L} \mu C_s (V_g - V_t) \quad (5.2)$$

From this formula the charge carrier mobility was calculated to be $1.3 \cdot 10^{-2}$ cm$^2$/Vs.

These I-V measurements were performed at various temperatures, from room temperature down to 145 K. In figure 5.4 the temperature dependence of the mobility is shown. Note that the range on the vertical scale is only 0.01 cm$^2$/Vs, which indicates that the mobility is almost temperature independent.
Figure 5.4: Mobility as function of temperature. The values are obtained from the I-V characteristics of a FET, with the 15.4 Å polymorph of pentacene as active layer.

5.2.3 Discussion

In organic TFTs a large variation in temperature dependence of the mobility has been observed, even in cases where the sample preparation conditions were held as constant as possible [10–13]. The behaviour varied from thermally activated to temperature independent. The transport properties in polycrystalline TFTs are generally believed to be dominated by impurities, disorder and grain boundary effects [8,10,14–19]. Recently SKB have reported an increasing mobility with decreasing temperature in pentacene, indicating band like conduction [20,21]. They observed this in both single crystals and polycrystalline TFTs of the 14.1 Å polymorph [21,22]. From the temperature independent behaviour of the mobility of the 15.4 Å phase it is not possible to determine what the fundamental transport mechanism is [10].

The differences are large, not only in the temperature dependence, but
also in the values observed for the mobility at room temperature. Recently very high mobilities were observed in pentacene TFTs, up to values observed for amorphous silicon (\(\sim 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\)) [21-24]. These mobilities are much higher than previously reported values for pentacene [17,25,26]. The observed differences in mobility are generally ascribed to differences in purity of the material, disorder and grain boundary effects [10,15,17,22].

Differences were observed between the mobilities of pentacene films deposited on substrates at room temperature, and on heated substrates [27,28]. These differences in mobility were ascribed to optimized ordering due to the applied heat [27,28]. The fact that there exists more than one polymorph of pentacene was until recently not recognised [29-31]. Therefore, the observed electronic properties are generally not related to a specific polymorph, and in most cases it is not even certain that the results were obtained from single phased samples. The existence of four different crystal structures of pentacene can be seen as an extra possibility to explain the observed differences in the mobilities of polycrystalline pentacene. The fact that the observed mobilities are dominated by disorder, and therefore not intrinsic, makes it very difficult to compare the values of the mobilities of the different crystal structures.

In general, caution should be taken in relating transport properties calculated from TFT I-V characteristics to a specific crystal structure. As we already mentioned, the electrical transport in a thin film transistor is not a bulk effect. The conduction takes place at the semiconductor - insulator interface, involving only the first monolayers in the charge transport. In studies of the growth mechanism of pentacene it is believed that the first layer of pentacene molecules lies flat on the substrate and interacts with the dangling bonds of the silicon surface [32]. In chapter 2, we showed that the middle ring of pentacene is quite reactive, and easily oxidises or hydrogenates. It can not be excluded that the initial pentacene layer at the interface has a different orientation, or that impurities are formed. This may have influence on the electrical properties.

### 5.3 Space-charge-limited conduction

In measurements of the current density, \(J\), as function of electric field, \(E\), on very pure single crystalline material four different current-voltage regimes
can be distinguished. From the trap-free space-charge-limited regime at high
electric fields, the bulk mobility of the material can be calculated.

5.3.1 Sample preparation

Samples for $J(E)$ measurements were prepared as follows. Single crystals
were grown under an argon or hydrogen atmosphere as described in chapter 2. Grown under a flow of argon the crystals were observed to have a
better developed $c^*$ direction, and the crystals were not electrically charged,
which was often the case for crystals grown under $H_2$ gas. Rectangular
shaped crystals were glued onto glass substrates using GE-varnish. Con-
tacts were applied using a shadow mask. Stripes of 10 nm titanium and
40 nm gold were evaporated in a high vacuum environment. Distances be-
tween the stripes were 50 or 75 $\mu$m. Measurements were performed in the $ab$
plane. Platinum wires were connected to the stripes with silver epoxy. The
epoxy was cured at 70°C in air for 10 minutes. The crystals were exposed
to air for approximately one hour before they were placed in vacuum.

Samples were measured in darkness and a vacuum of $2 \times 10^{-7}$ mbar. As
measuring device a Keithley 2410 high voltage sourcemeter was used. Some
measurements were performed in air, using a home build probe station. The
$J(E)$ characteristics were measured using a pulsed staircase sweep with a
pulsewidth of 0.3 sec.

5.3.2 Measurements

The curve in figure 5.5 is typical for crystals measured in air. The cur-
rent density was determined to be proportional to $V^{2.2}$. To determine the
trap distribution responsible for this behaviour, the temperature dependence
should be measured. The trap filling limit was reached in none of the mea-
surements in air.

In a high vacuum of $2 \times 10^{-7}$ mbar different behaviour was observed.
The curves in figure 5.6 and 5.7 show an ohmic and a space-charge-limited
regime, and reach the trap filling limit at $10^5$ V/cm.

The curves in figure 5.6 were measured with increasing and with decreas-
ing electric field, showing that the 'jump' in the curve was not due to heating
effects. The reproducibility of the measurements was rather low. After two
measurements we had to wait at least 12 hours before the trap filling limit
could again be observed. Large differences could be observed in one crystal. On one pair of stripes on the crystal a curve like in figure 5.7 was measured, 200 µm further the trap filling limit was not reached at all.

The curves in figure 5.7 are more clear. Better characteristics than represented by the circles (●) could not be observed, since the current became larger than the highest range of the sourcemeter (which is the case for ■). The same occurs when we cool the sample: we can not measure beyond the trap filling limit. Interesting is the difference in shape of the different curves. The second curve (■) shows a sharper transition between the ohmic and the space-charge-limited regime than both other curves. Although we have little statistics, it seems that the reproducibility becomes higher as quality of the sample is higher.

All results presented so far originate from measurements on single crystals grown under argon flow. Crystals grown under a hydrogen flow\(^1\) were also measured, but no trap filling limit could be observed. This indicates that these crystals do not have the same high quality.

\(^1\)The crystal growth is explained in detail on page 14.
Figure 5.6.: Current-voltage characteristics of single crystalline pentacene. ■: measured with increasing electric field strength, •: measured with a decreasing electric field. The measurements were performed in vacuum and darkness.

5.3.3 Analysis and discussion

The results of the current-voltage measurements can be described using the standard semiconductor band model [33]. In the graphs four distinct regimes can be observed, see figure 5.8. At low electric fields the current is ohmic, rising linearly with the electric field. At higher electric fields the current becomes space charge limited and reaches eventually the point where all traps are filled. The charge carrier mobility can be determined from the trap-free space-charge-limited current above this trap-filling limit. We assume holes to be the majority carriers in the crystals. In the ohmic regime the current density is given by:

\[ j_\Omega = e\mu p \frac{V}{L} \]  

(5.3)
with $e$ the electronic charge, $\mu$ the charge carrier mobility, $V$ the applied voltage, $L$ the distance between the contacts and $p$ the hole density. If we assume a discrete shallow trap distribution, $p$ is:\(^{[2]}\)

$$p = \frac{N_v N_a}{N_t} e^{-E_t / k_B T} \quad (5.4)$$

$N_v$ is the effective density of states in the valence band, $N_a$ the acceptor density, $N_t$ the trap density, $E_t$ the energy of the trap level, $N_v$ is assumed to be one state per molecule, $4.3 \cdot 10^{21}$ cm$^{-3}$ for pentacene [34].

If, again, a discrete trap-level is assumed the current density in the space-charge-limited regime can be described as:

\(^{[2]}\)The validity of this assumption can be checked by measuring the temperature dependence of the SCLC curves.
5.3 Space-charge-limited conduction

Figure 5.8: Current density vs. electric field. The solid lines represent the fits of the four different regimes.

\[ j_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \Theta \mu \frac{V^2}{L^3} \]  

(5.5)

with \( \varepsilon_0 \) the permittivity of free space and \( \varepsilon_r \) the relative dielectric constant of pentacene (assumed to be 3). The ratio of the number of free carriers to the total number of carriers is given by \( \Theta \):

\[ \Theta = \frac{g_p N_v}{N_i} e^{-E_t/k_B T} \]  

(5.6)

with \( g_p \) the degeneracy factor of the hole trapping states, generally 1/2 [35,36]. If the trap level is not assumed to be discrete but to be an exponential, Gaussian, or uniform distribution, the current density will not be proportional to \( V^2 \). In those cases the power will be larger than 2 and depends on the temperature [33].
The voltage of the trap filling limit is given by:

\[ V_{TFL} = \frac{2eL^2N_t}{3\varepsilon_0\varepsilon_r} \]  

(5.7)

Assuming the mobility to be independent of the applied electric field, the current density in the trap-free space-charge-limited regime is given by the Mott-Gurney equation (which can be derived from Poisson’s equation):

\[ j_{SCLC,TF} = \frac{9}{8\varepsilon_0\varepsilon_r\mu} \frac{V^2}{L^5} \]  

(5.8)

From these equations we calculated the hole mobility, trap density, the energy of the trap level and the acceptor density. The results are listed in table 5.1.

<table>
<thead>
<tr>
<th>( \mu ) [cm(^2)/Vs]</th>
<th>( N_t ) [cm(^{-3})]</th>
<th>( E_t ) [meV]</th>
<th>( N_a ) [cm(^{-3})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 5.7 ▲</td>
<td>0.17</td>
<td>2 ( \cdot ) 10(^{13})</td>
<td>580</td>
</tr>
<tr>
<td>Fig. 5.7 ■</td>
<td>&gt; 0.2</td>
<td>1 ( \cdot ) 10(^{13})</td>
<td>-</td>
</tr>
<tr>
<td>Fig. 5.7 ●</td>
<td>0.15</td>
<td>1 ( \cdot ) 10(^{13})</td>
<td>560</td>
</tr>
<tr>
<td>SKB [34]</td>
<td>1.4</td>
<td>6 ( \cdot ) 10(^{14})</td>
<td>650</td>
</tr>
</tbody>
</table>

Table 5.1.: Electrical properties of pentacene single crystals obtained from SCLC analysis.

These SCLC measurements show that our single crystals exhibit a mobility (0.2 cm\(^2\)/Vs) that is little lower than the highest reported values for pentacene, 2 cm\(^2\)/Vs. The crystals are very pure, having only 10\(^{13}\) traps cm\(^{-3}\). This value is in between the values reported by SKB [1,34] for their pentacene crystals: 3 \( \cdot \) 10\(^{12}\) - 6 \( \cdot \) 10\(^{14}\). It is, however, strange that the use of H\(_2\) gas during the growth was reported to be essential for the reduction of traps [1], while we obtained our best results on crystals grown under an argon atmosphere. The fact that we were not able to reach the trap filling limit in crystals grown under H\(_2\) flow, made us believe that hydrogen forms an origin of traps in the crystals. This shows that the influence of the transport gases, especially H\(_2\), on the purity of the crystals is not obvious and needs further investigation.
5.4 Band structure

Recently SKB [1] reported transport measurements on single crystalline pentacene. Using SCLC measurements, the mobility was determined as function of temperature for different crystallographic directions. They observe an anisotropy of the mobility in the ab plane as well as for the c* direction. We show their results for the ab plane in figure 5.9. From their measurements also the effect of the electric field on the mobility could be studied by calculating the hole velocity \( v_h = \mu(E)E \). They observe a saturation of the hole velocity, which is explained by assuming a non-parabolic valence band.

![Diagram](image)

Figure 5.9.: Room temperature hole mobility within the ab plane of single crystalline pentacene. Data taken from Schön, Kloc and Ballegg: Phys. Rev. B, V63, p.245201-10, 2001.

At high electric fields the charge carriers can reach a region in the energy band with a high effective mass, which limits the carrier velocity. Warta and Karl [20] proposed such a model in their study of naphthalene. This model
allows SKB to make an estimate for the band width of the valence band in pentacene, based on the observed hole velocity saturation. They observe a strong temperature dependence of the hole velocity.

This implies that also the band width is depending on the temperature. To account for the temperature dependence thermal expansion alone was not enough, so electron-phonon interaction was taken into account. The electron-phonon coupling constant is shown to be essentially independent of the direction in the pentacene layer. From the calculated band width also the effective mass is calculated [37]. Using the effective mass an estimate for the relaxation time is made: \( \tau(T) = \mu m^*/e \).

It is of interest to relate the observed anisotropy to the crystal structure, to understand why the transport differs for the different crystallographic directions. In order to get some insight, we calculate the electronic band structure of pentacene, both for one layer of molecules and for the single crystal structure. The band structure is fitted using a tight-binding model. From the tight-binding fit of the band structure we calculate the effective mass for various directions. The results are compared to the data of SKB.

### 5.4.1 Method: DFT

The electronic band structure of pentacene was calculated using density functional theory (DFT). DFT calculates the ground state properties of a many-body system [38,39]. DFT is based on two theorems of Hohenberg and Kohn: The ground state energy, \( E \), for a given external potential of a many-body system, can be expressed as a functional of the electronic charge density, \( \rho(r) \). The second theorem states that the ground state energy and density are obtained by minimization of the energy functional. Thus, DFT avoids the calculation of the wave functions of the system.

To obtain a workable scheme, a good approximation to the (unknown) functional is needed. This was achieved by Kohn and Sham. They wrote the density in terms of non-interacting KS-orbitals \( \{ \phi_{i,k}^{KS} \} \), where \( i \) labels the bands and \( k \) the \( k \)-points. Thus, the kinetic energy part of the functional is easily calculated. The electrostatic part (Hartree) is also straightforward. For the remaining exchange and correlation contributions a good approximation was found in the local density approximation (LDA). The LDA replaces the exchange correlation energy of the system locally with the exchange
5.4 Band structure

The correlation energy of a homogeneous electron gas with the same density:

\[ E_{xc}[\rho(r)] = \int d^3 r \rho(r) \epsilon_{xc}(\rho(r)) \]  

(LDA is a local approximation. The generalized gradient approximation (GGA) also takes the gradient of the density into account.

The minimization can be reformulated in terms of the eigenvalue equation:

\[ (-\frac{k^2}{2m} \nabla^2 + V_{\text{eff}}(r)) \psi_{i,k}^{KS} = \varepsilon_i \psi_{i,k}^{KS} \]  

which, as \( V_{\text{eff}} \) depends on \( \rho \), has to be solved self consistently.

An extensive overview of the density functional formalism is given by Jones and Gunnarsson [38].

5.4.2 Computational details

The calculations have been performed using the \emph{ab initio} total-energy and molecular-dynamics program VASP (Vienna \emph{Ab initio} Simulation Program) developed at the Institut für Theoretische Physik of the Technische Universität Wien [40-43]. The calculations were done in the generalized gradient approximation (GGA) and the gradient corrections following Perdew et al. (PW91) were adopted [44].

The band structure was calculated for the single crystal unit cell as determined at 90 K\(^{(3)}\) using periodic boundary conditions to form a crystal. Calculations were also performed for one layer of pentacene molecules. In this case a cell was constructed by putting the layers of molecules 6 or 11 Å further apart than in the single crystal. The molecules in the different layers were placed above each other, forming a monoclinic unit cell. At approximately 4 eV above the Fermi level the DOS of the case with 11 Å between the layers started to differ from the cell which had a 6 Å layer spacing. This indicates that the layer spacing we introduced is large enough to exclude effects of the next layer.

For the density of states (DOS) calculation a 4×4×2 \( k \)-point mesh [45] and tetrahedron interpolation [46] were used. To test whether this were

\(^{(3)}\) Observed unit cell parameters and fractional coordinates at 90 K are listed in appendix B.
enough points, we also employed a mesh of $6 \times 6 \times 4$. The total energy difference between both calculations was only 0.1 meV/cell, indicating the $4 \times 4 \times 2$ mesh to be dense enough. $\Gamma$ was chosen to be on the mesh.

The KS-orbitals were expanded in plane waves. Electron-ion interactions were described using the projector augmented-wave (PAW) method [47,48]. No core electrons, but only the valence band states were considered. The kinetic energy cut-off on the wave functions was chosen 500 eV and on the augmentation charge density 650 eV.

5.4.3 Results

Density of States

In figure 5.10 the calculated density of states (DOS) is shown as function of the energy. The energy is chosen to be zero at the top of the valence band. The DOS is shown for two cases: for the single crystal structure and for one layer of pentacene molecules (with 6 Å extra layer spacing). They seem to be identical until approximately 3 eV above the Fermi level. In the following we will therefore first consider the case of one layer of pentacene molecules.

From the calculations of the DOS, the band widths of the HOMO and LUMO levels were determined to be approximately 600 meV and 700 meV, respectively. This is in qualitative agreement with both SKB papers [1,49]. The results agree also very well with other recent theoretical calculations for the valence and conduction band widths of 608 and 588 meV, respectively [50]. However, band widths of 600 meV and 700 meV are much larger than earlier estimates for pentacene, of 11 and 14 meV [20,51].

The gap between the HOMO and LUMO level was calculated to be 0.7 eV. This is much lower than the measured value for pentacene, which is 2.2 eV [52]. This is not unusual for DFT-GGA calculations [38].

In order to investigate the effect of the presence of the H atoms, we performed another calculation. The carbon atoms which are bonded to a hydrogen atom, were, together with the hydrogen atoms, replaced by nitrogen atoms on the carbon site. In this way the hydrogens are removed, but the number of electrons stays the same. The band structure was calculated. The band that corresponds to the HOMO of pentacene was identified in the new band structure. The observed bands were narrower than in the band structure of single crystalline pentacene, especially in the $c^*$ direction.
Figure 5.10: Density of states in states per eV per cell as function of the energy. The energy is chosen zero at the top of the valence band. Solid line: single crystal, dotted line: cell with the molecules 6 Å apart. Both curves are calculated using a 4×4×2 mesh. IDOS is the integrated DOS in states(electrons) per cell.

This indicates that the hydrogen atoms play an important role, since they significantly contribute to the size of the HOMO. That the band width decreases in particular in the direction of c*, indicates that the hydrogen atoms are especially important for the interlayer interactions. However, it can be objected that the nitrogen wave functions are somewhat smaller than the wave functions of the carbon atoms. This can also cause the band widths to decrease slightly.

Another way to observe the effect of the hydrogen atoms is to study the
partial contributions of the different orbitals to the density of states. Projections onto spherical harmonics have been carried out in spheres with radii of 0.86 and 1.00 Å for C and H, respectively. The resulting contributions of the s, p, and d orbitals of the carbon and hydrogen atoms are depicted in figure 5.11. It can be seen that the hydrogen p orbitals contribute significantly to the density of states at the Fermi level. This is consistent with the previous observation, where we removed the hydrogens and calculated the band width. We already used the fact that the hydrogen atoms play an important role in chapter 3. In one of the models we used there, we calculate the overlap of the hydrogen 2p orbitals with the HOMO of a neighbouring molecule.

Band structure of one layer of molecules

The only symmetry present in the pentacene single crystal structure is inversion symmetry. In reciprocal space, the points between the inversion centers (halfway between $\Gamma - \Gamma$): (1/2, 1/2, 0), (0, 1/2, 0) and (1/2, 0, 0) will therefore also have inversion symmetry. We choose to show the dispersion in these directions of the structure. The band structure calculated for one layer of pentacene molecules (i.e. with an extra layer spacing of 6 Å) can be seen in figure 5.12.

SKB [1] estimate the band width for a number of crystallographic directions. At low temperatures the effective band width for the a and b axis are $\sim 0.3$ eV and $\sim 0.35$ eV. This is however, in presence of electron-phonon interactions. For the electronic band width in absence of these interactions 0.6 and 0.7 eV are reported for the b and d (d represents a + b) direction, respectively. This is in good agreement with the band widths we calculated.

Our calculations show that from the top of the valence band, $M$, the dispersion in the $b^*$ direction is larger than in the $a^*$ direction. Therefore, the effective band width in the b direction is expected to be larger than in the a direction.

\(^{(4)}\) The radius of the sphere for the H atom was taken rather large (it even touches the carbon atom), since we want to observe the 2p states. The maximum of the radial function lies at 1.00 Å, so this seems a logic choice.

\(^{(5)}\) The assumptions on which this estimate is based are mentioned at the beginning of section 5.4.
5.4 Band structure

Figure 5.11.: The density of states in states per eV per unit cell as function of the energy. The energy was chosen to be zero at the top of the valence band. The figure shows in different graphs the contributions of the $H$ s, p and d and $C$ s, p and d states to the total density.

Tight-binding fit

The tight-binding approximation approaches the solid as a collection of weakly interacting molecules. It treats the system as isolated molecules, with a term for the overlap of the molecular orbitals. We used this model to fit the band structure. Within the tight-binding formalism, the energy is
Figure 5.12.: The band structure of one layer of pentacene molecules, with a layer spacing of 6 Å. The energy is chosen to be zero at the top of the valence band. The energies are plotted along lines in the first Brillouin zone, connecting the points $\Gamma = (0,0,0)$, $X = (a^*/2,0,0)$, $M = (a^*/2,b^*/2,0)$, and $Y = (0,b^*/2,0)$. From $\Gamma$ to $M$ is in the direction of $1/2(a^* + b^*)$, from $M$ to $\Gamma$ is from $1/2(a^* - b^*)$ to $\Gamma$. The solid line is the tight binding fit.

described by:

$$\varepsilon(k) = E_A + \sum_{\mathbf{R}} \gamma(\mathbf{R}) \cos(\mathbf{k} \cdot \mathbf{R})$$  \hspace{1cm} (5.11)

with $E_A$ a molecular energy, $\mathbf{k}$ the reciprocal space lattice vectors, $\mathbf{R}$ the direct lattice vectors and $\gamma$ the overlap integral:

$$\gamma(\mathbf{R}) = -\int d\mathbf{r} \phi^*(\mathbf{r}) \Delta U(\mathbf{r}) \phi(\mathbf{r} - \mathbf{R})$$  \hspace{1cm} (5.12)
5.4 Band structure

where $\Delta U(r)$ plus the molecular potential is the periodic potential of the crystal.

In the case of pentacene we have to take into account that the two molecules in the unit cell are inequivalent. We can express this problem as a $2 \times 2$ matrix, which we diagonalize to obtain the eigenvalue spectrum. The matrix will have the general form:

$$
\begin{bmatrix}
\varepsilon(k) - e_1 - T_1 & T_2 \\
T_2 & \varepsilon(k) - T_1
\end{bmatrix},
$$

with $\varepsilon(k)$ the energy, and $e_1$ accounts for the fact that not both pentacene molecules in one unit cell are equivalent. $T_1$ represents the sum of the overlap integrals for the overlap between the equivalent molecules, $T_2$ is the overlap term for the overlap between the inequivalent molecules. This gives two possible solutions for $\varepsilon(k)$, resulting in two bands.

Tight binding fits were made for both the HOMO and LUMO level of the band structure. The result is shown as the solid line in figure 5.12. Into the fit the following sums of overlap integrals enter:

$$
T_1 = 2 \; t_a \cos(k \cdot a) + 2 \; t_b \cos(k \cdot b) + 2 \; t_{2a} \cos(k \cdot 2a) + 2 \; t_{a+b} \cos(k \cdot (a+b)) + 2 \; t_{a-b} \cos(k \cdot (a-b))
$$

and

$$
T_2 = 2 \; t_{(a+b)/2} \cos(k \cdot (a+b)/2) + 2 \; t_{(a-b)/2} \cos(k \cdot (a-b)/2) + 2 \; t_{3(a+b)/2} \cos(k \cdot 3(a+b)/2) + 2 \; t_{3(a-b)/2} \cos(k \cdot 3(a-b)/2)
$$

Sets of fitting parameters were obtained for the HOMO and LUMO independently, see table 5.2. Three parameters appear to be most important (both for the HOMO and LUMO): $t_a$, $t_{(a+b)/2}$ and $t_{(a-b)/2}$. These transfer integrals can be associated with the directions $a$, $a+b$ and $a-b$ in the crystal structure, see figure 5.13.

The resulting difference in energy, $e_1$, between the two molecules is 42 meV and 47 meV, for the HOMO and LUMO level, respectively. The transfer integrals of the HOMO level have the following energies, $t_a = 31$ meV, $t_{(a+b)/2} = -56$ meV and $t_{(a-b)/2} = 91$ meV. For the LUMO the values are: $t_a = -41$ meV, $t_{(a+b)/2} = -90$ meV and $t_{(a-b)/2} = 90$ meV.

Brédas et al. performed semi-empirical Hartree-Fock INDO calculations, which indicated the same directions to be of importance [53]. For the HOMO level their transfer integrals were calculated to have the following values: $t_a =$
47 meV, \( t_{d1} = 80 \text{ meV} \) and \( t_{d2} = 72 \text{ meV} \). For the LUMO they reported: \( t_a = 47 \text{ meV} \), \( t_{d1} = 59 \text{ meV} \) and \( t_{d2} = 88 \text{ meV} \). Their \( d_1 \) direction corresponds to our \( a + b \) direction and \( d_2 \) to \( a - b \). For the energy difference between the molecules they reported 61 meV (HOMO) and 70 meV (LUMO). Brédas et al. do not report the signs of their parameters, but the absolute values are of the same order of magnitude.

We now try to understand the relative magnitude and sign of the relevant transfer integrals. Considering the electron density of the HOMO-level of a pentacene molecule (see page 52), we infer from its shape that the overlap will be larger in the case the molecules are not shifted. In this way it can be understood that the overlap for the \( a - b \) direction is larger than for \( a + b \), so: \(|t_{(a-b)/2}| > |t_{(a+b)/2}|\). In case of the LUMO of the pentacene molecule this is less clear. The ends of the molecules do not seem to take part in the overlap, in case the molecules are not shifted. In case the molecules are shifted, it is possible that also the ends participate in the overlap. The fact that we find the overlap integrals \(|t_{(a+b)/2}|\) and \(|t_{(a-b)/2}|\) almost equal is therefore not unreasonable. That \( t_{(a+b)/2} \) and \( t_{(a-b)/2} \) have opposite sign, for both the HOMO and LUMO, is also a consequence of their relative shifts. We observe that \( t_{(a+b)/2} \) and \( t_{(a-b)/2} \) have the same sign for both HOMO
Table 5.2.: The overlap integrals that were used for the tight binding fit. The values are in electron volts, and are given for the fits of both bands, HOMO and LUMO.

and LUMO, while \( t_a \) has opposite sign for HOMO and LUMO.

The top and the minimum of the valence band do not lie at \( \Gamma \), but at \( M, (a^*/2, b^*/2, 0) \). The point \( M \) lies at the Brillouin zone corner: the atomic orbitals will have, both after a translation in the \( a \) and \( b \) direction, the opposite phase. The wave functions at \( M \) are shown in figure 5.14. Translations along \( a \) and \( b \) do not seem to result in an opposite phase. However, we recall from chapter 3 that the molecules are shifted with almost one benzene ring along their length axis when crossing the step in the \( a + b \) direction (indicated by the dotted lines in the figure). This effectively amounts to an extra phase change with 180°. As a final result the situation depicted in figure 5.14 emerges.

The phase of the inequivalent molecule is not fixed and may be chosen freely. Both possibilities are shown in figure 5.14. For one choice all orbitals, in the directions \( a \), \( a + b \) and \( a - b \) are bonding. This maximum bonding situation agrees with the fact that the minimum of the valence band is located at \( M \). The phase of the inequivalent molecule can also be chosen opposite. This gives the situation that all orbitals except for the overlap in
Figure 5.14.: The ab plane of pentacene. The HOMO wave functions are schematically depicted with the + and - signs to indicate the phase (see chapter 3). On the left the most antibonding situation, as is the case at the top of the valence band. On the right all orbitals are bonding, forming the bottom of the valence band. The dashed lines indicate the shifts between the molecules.

the a direction are antibonding. This is the most antibonding situation possible, which agrees with the fact that M forms the top of the valence band. In the a direction the orbitals are bonding, while the a − b and a + b direction are antibonding. This gives rise to frustration in the a direction, which is revealed in the very flat band in the a* direction (M − Y), see figure 5.12.

Effective mass

In the following we will study the effective mass anisotropy in the pentacene layer and compare it to the experimental results of SKB. From the top of the valence band the hole effective mass, \( m^* \), can be calculated by:

\[
- \frac{\partial^2 \varepsilon(k)}{\partial k^2} = \frac{\hbar^2}{m^*}
\]  

(5.13)

Using the tight-binding fit the effective mass could be calculated for all directions in the a\( \overline{b} \) plane. The effective mass is related to the mobility by:
5.4 Band structure

\[ m^* = \frac{e^2}{\mu} \]

The results are presented in figure 5.15, where the reciprocal effective mass is shown as function of the crystallographic direction. The smallest value for the effective mass, 1.6 \( m_e \), was observed for the direction \( \mathbf{b}^* \), which is therefore the most mobile direction.\(^6\) The largest value of the effective mass, 58 \( m_e \), was observed for the \( \mathbf{a} \) direction.

We want to compare the calculated results to the experimental data. SKB determined the effective mass from Shubnikov-de Haas oscillations, at low temperature [49], but no anisotropy was reported for these measurements. A comparison can be made with the effective mass which is

\[^6\] As mentioned in section 5.4.2, these calculations are performed on one layer of pentacene molecules, placed in a monoclinic unit cell with \( \gamma \neq 90^\circ \). The \( \mathbf{a}^* \) and \( \mathbf{b}^* \) direction lie, therefore, also in the \( ab \) plane.
determined by SKB from SCLC measurements [1]. Their effective mass is derived from a model that assumes a non-parabolic band and, as a result, an anisotropic relaxation time $\tau$. This model assumes a simple, cosine-shaped band [20]. Below, we will see, however, that the calculated band structure is more complicated. In particular, the dispersion in the $a^*$ direction strongly deviates from this simple form. Therefore we think it is better to make a more direct comparison with SKBs experiments and compare to their mobility measurements. Comparison with figure 5.9 is not possible, since the band structure was calculated for the electronic groundstate, i.e. the limit $T \to 0$ K, while the mobility of SKB is measured at room temperature. For the directions $a$, $b$, $c^*$ and $d$, however, also low temperature (30 K) data are available [1].

In order to be able to compare to our calculated effective mass the mobility data are not enough: we also need a relaxation time, $\tau$. For consistency we cannot take SKBs data from Ref. [1] as these are based on data derived from the non-parabolic band model. Instead we take their $\tau$ from Ref. [54] and assume it to be isotropic. That value of $\tau$ pertains to a temperature of 1.7 K. We make a rough estimate by rescaling the value observed at 1.7 K [49,54], to 30 K by multiplying with $(30/1.7)^{-2}$. In this way the anisotropy ratio of the effective mass will be the reciprocal of that of the mobility, since $m^* = e\tau/\mu$. The following effective masses result from the mobility data of Ref. [1] (at 30 K) and the rescaled $\tau$: $m^*_{a} = 4.3$ me, $m^*_{b} = 0.7$ me, and $m^*_{d} = 0.7$ me. Thus we derive an anisotropy ratio $m^*_{a}/m^*_{b} = 6$ for the measurements of SKB, whereas we calculated a ratio of $m^*_{a}/m^*_{b} = 36$. We observe that the difference in mobility between the $b$ and $d$ direction is negligible. Our most mobile direction is $b^*$, a direction which lies very close to $b$. Therefore, we see no objection to compare the ratio $m^*_{a}/m^*_{b}$ to $m^*_{a}/m^*_{b}$. The difference between the calculated and measured anisotropy ratio is very large. A contribution to the interactions in pentacene is due to the van der Waals interaction. In the framework of intermolecular perturbation theory three contributions to these weak van der Waals interactions are discerned [55–57]. Firstly, the electrostatic interaction between the frozen charge densities of the isolated molecules. Secondly, a single excitation term, in which the excited states on only one molecule are considered. This so-

(7) Here we used the derived temperature dependence of the relaxation time of SKB [1]. The factor of 2 is an average over the $a$ and $b$ direction.
5.4 Band structure

called induction term reflects the response of one molecule to the static field of the other. And thirdly, a double excitation term, in which local excitations on both the interacting molecules are considered. This term, describing the dynamical interaction of induced dipoles, accounts for the London dispersion interaction. DFT-GGA describes the first well, and the second reasonably well. However, the latter is practically missing. Indeed, DFT-GGA calculations for benzene give unphysical results, whereas a correction for the missing London dispersion force produces a reasonable dimer geometry [58]. The London dispersion interaction leads to an increase in band width and a corresponding decrease in effective mass, as was observed for polythiophene and PPV [59]. Since there is no reason to assume a priori that the London interaction is strongly anisotropic in the ab plane, its inclusion will reduce the calculated anisotropy in the ab plane.

We ascribe our large anisotropy ratio to the missing London dispersion interaction. We make an estimate for the relative strength of this interaction. The carriers are most mobile in the b* direction, thus the contribution of the London dispersion interaction to this direction is relatively small. However, the effective mass in the a direction is very large. (Indeed, it is an order of magnitude larger than all estimates by SKB). An added dispersion interaction will for this direction determine the value of the effective mass. To obtain an anisotropy ratio of 6, as observed by SKB, we have to assume an effective mass of 10 m_e for the a direction. Assuming a cosine-shaped band, we estimate that an extra band width of 0.019 eV will be enough to reduce our calculated anisotropy to the ratio of SKB. This is a reasonable value.

We estimate this extra band width under the assumption that we do not have to take the electron-phonon contribution into account, but one may question whether this is right. As mentioned by SKB [1], the electron-phonon coupling constant is essentially independent of direction within the molecular layer. We base our estimate of the effect of the London dispersion interaction on the anisotropy ratio. Here the electron-phonon coupling constant drops out and we may assign our calculated value to the experimental value. The electron-phonon coupling will, however, have to be taken into account to obtain absolute values of the effective mass.

SKB report, using their non-parabolic band model, an effective mass of \( \sim 1.0 \, m_e \) for the d direction (at 30 K). From our estimates, assuming an isotropic \( \tau \), the effective mass will be 0.7 \( m_e \). Our calculated effective mass
for that direction is 2.2 m_e. This bare value is still enhanced by the electron-
phonon interaction. However, as we will see in the next section, we expect
this interaction to be most important in the e^* direction. We can speculate
about the origin of the discrepancy. To obtain the value of 0.7 m_e we assumed
\( \tau \) to be isotropic and used a rough method to scale the value obtained for
1.7 K to 30 K. SKB derive the 1.0 m_e value from a saturation of the hole
velocity, for which extremely high electric fields (6 m V/\AA) have to be applied.
Effects of such high fields on the band structure have not been accounted for.
So, care is needed to make a direct comparison. Indeed, for the \( a^* \) direction
such fields become comparable to the estimated correction to the band width
for the London dispersion interaction. Moreover, for this direction the band
is not of a simple cosine shape. For a consistent interpretation of the data
a generalization of the non-parabolic band model [20] to account for more
complicated bands than those of simple cosine shape (and finite fields) seems
desirable.

**Band structure of single crystalline pentacene**

So far, we considered the band structure calculated for one layer of pentacene
molecules. The band structure was also calculated for the pentacene single
crystal. The results can be seen in figure 5.16. The band structure for the
points in the \( a^*b^* \) plane is not very different from the calculations on one
layer of molecules. However, the top of the valence band does not lie at \( M \).
The \( k \)-point (0.375, 0.5, 0.075) forms the top of the valence band. This point
lies very close to \( M \), in an area where the band is no longer parabolic, as can
be seen from the top graph in figure 5.16.

A tight-binding fit was performed for the band structure, the resulting
overlap integrals are listed in table 5.3. The most relevant integrals in the
band structure of one layer of molecules were \( t_a, t_{(a-b)/2} \) and \( t_{(a+b)/2} \). The
values of \( t_{(a-b)/2} \) and \( t_{(a+b)/2} \) are unchanged with respect to this case, so
these overlap integrals are still the largest in the single crystal structure. The
band structure shows for the \( a^* \) direction non-parabolic behaviour, a tight-
binding fit was therefore problematic for this direction. It is probable that
this is the reason why a different value for the overlap integral \( t_a \) is observed.
Since the fit broke down, the effective mass was calculated directly from the
band structure using finite differences. The results are plotted as function
of the direction in figure 5.17. For the directions that could be calculated,
5.4 Band structure

Figure 5.16.: The band structure of single crystalline pentacene. The energy is chosen to zero at the top of the valence band. The energies are plotted along lines in the first Brillouin zone, connecting the points $\Gamma = (0,0,0)$, $X = (a^*/2,0,0)$, $M = (a^*/2,b^*/2,0)$, $Y = (0,b^*/2,0)$, $Z = (0,0,c^*/2)$, $N = (0,b^*/2,c^*/2)$, $H = (a^*/2,b^*/2,c^*/2)$ and $O = (a^*/2,0,c^*/2)$. From $\Gamma$ to $M$ is in the direction of $1/2(a^* + b^*)$, from $M$ to $\Gamma$ is from $1/2(a^* - b^*)$ to $\Gamma$. The solid line is the tight binding fit. The top graph shows an enlargement of the top of the valence band.

the results are in good agreement with the results as presented for the band structure calculated for one layer of molecules. For the $a^*$ direction we still believe that the picture we outlined earlier (for one layer of molecules) holds, since the extra bump at $(0.375, 0.5, 0.075)$ is extremely small, and effectively
Table 5.3.: The overlap integrals that were used for the tight binding fit of the band structure calculated for single crystalline pentacene. The values are in electron volts.

<table>
<thead>
<tr>
<th></th>
<th>HOMO [eV]</th>
<th>HOMO [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_1$</td>
<td>0.022</td>
<td>$t_{(3a+b)/2}$</td>
</tr>
<tr>
<td>$t_a$</td>
<td>0.031</td>
<td>$t_{(3a-b)/2}$</td>
</tr>
<tr>
<td>$t_b$</td>
<td>-0.001</td>
<td>$t_{b+c}$</td>
</tr>
<tr>
<td>$t_c$</td>
<td>0.002</td>
<td>$t_{a+b+c}$</td>
</tr>
<tr>
<td>$t_{2a}$</td>
<td>-0.001</td>
<td>$t_{3(a+b)/2}$</td>
</tr>
<tr>
<td>$t_{(a+b)/2}$</td>
<td>-0.057</td>
<td>$t_{3(a-b)/2}$</td>
</tr>
<tr>
<td>$t_{(a-b)/2}$</td>
<td>0.090</td>
<td>$t_{(3a+b+2c)/2}$</td>
</tr>
<tr>
<td>$t_{a+b}$</td>
<td>0.001</td>
<td>$t_{(a+3b+2c)/2}$</td>
</tr>
<tr>
<td>$t_{a-b}$</td>
<td>0.002</td>
<td>$t_{3(a+b)/2+c}$</td>
</tr>
<tr>
<td>$t_{a+c}$</td>
<td>0.002</td>
<td></td>
</tr>
</tbody>
</table>

The effective mass was also calculated for the $c^*$ direction: $m_{c^*} = 5.2$ $m_e$. If we assume an isotropic relaxation time, and use SKBs mobility data, we expect a very large effective mass for this direction of $50$ $m_e$. In this case our calculated value is indeed lower than the estimate from the mobility. The layered structure of pentacene may offer an explanation. In the $c^*$ direction, the molecules interact in a 'head on' fashion with a hydrogen-hydrogen contact as weakest link. Whereas within the layers the herringbone structure allows the hydrogens to interact with a delocalized planar $\pi$ system. In section 5.4.3 we observed that the hydrogen atoms play an important role for the HOMO, and especially in the $c^*$ direction. Being the lightest element, the hydrogens are much affected by zero-point vibrations. Their zero-point motion can cause a decrease of the mobility, as the overlap between neighbouring molecules is affected. This is particular severe for the $c^*$ direction.

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(8) Given the large applied electric field, this feature might be washed out completely.
Figure 5.17.: The reciprocal effective mass as function of the crystallographic direction. Calculations are based on the band structure of single crystalline pentacene. The pentacene molecules are shown as reference to the crystallographic directions.

5.5 Conclusion

Polycrystalline thin films of the 15.4 Å phase of pentacene were grown and used as the active layer in a thin film transistor. The I-V characteristics of the TFT were analyzed, and the mobility was determined to be $1.3 \cdot 10^{-2}$ cm$^2$/Vs. This measured mobility was observed to be temperature independent. Generally, thermally activated behaviour is observed in this type of experiments [27]. Various hopping models have been proposed to explain the observed temperature dependences [14,27]. Temperature independent behaviour, however, excludes hopping as transport mechanism. Recently a pentacene thin film transistor was observed to have an increasing mobility with decreasing temperature [21]. Both temperature independent and activated behaviour are generally ascribed to the presence of grain boundaries and impurities in the material [10,14,17,19]. It is therefore not
possible to determine the intrinsic charge transport mechanism for this film. The charge transport of single crystalline pentacene was determined using two-point I-V measurements with very high electric fields. These space-charge-limited-current measurements showed the crystals to be of high quality, with only $10^{13}$ traps cm$^{-3}$. The observed mobility was, however, not so high as the mobilities reported by Schön, Kloc and Batlogg [1]. A striking observation is that it was reported to be essential for the quality of the crystals that they were grown under a flow of H$_2$ gas. We observed, however, that crystals grown under Ar-gas gave results that were far better than our hydrogen-grown crystals. Based on this observation and the fact that pentacene is sensitive to both oxidation and reduction (see chapter 2), we suggest that hydrogen forms a source of traps in the crystals. However, hydrogen may be essential for passivating the surface.

In order to get insight into the anisotropy of the mobility as observed by SKB [1], we calculated the electronic band structure of pentacene using DFT. The calculations were performed for two cases: firstly for one layer of molecules, and secondly for single crystalline pentacene. The observed band widths of the HOMO and LUMO were 0.6 and 0.7 eV, respectively, which is in good agreement with estimates based on experiments [49]. The band structure of one layer of pentacene molecules could be fitted using a tight binding model. The resulting overlap integrals indicated the $a$, $a + b$ and $a - b$ direction to be of main importance. We have shown that the values of these parameters and the position of the top of the valence band can be understood in terms of the phase of the wave functions and the shift of the molecules. From the band structure at the top of the valence band the effective mass was calculated. The result was compared to the literature. We observed that the direction of the highest mobility did not entirely agree with the measurements of SKB, although the directions did not differ much. However, we observed a large difference in the anisotropy ratio. We ascribe this difference to the London dispersion interaction, which is omitted in the DFT-GGA calculations. The band structure calculations of single crystalline pentacene showed results that were comparable to the results obtained for one layer of molecules.
References

References

References

References