Doctoral Thesis

Crystal structure analysis and trap spectroscopy in organic semiconducting crystals

Author(s):
Haas, Simon

Publication Date:
2006

Permanent Link:
https://doi.org/10.3929/ethz-a-005217957

Rights / License:
In Copyright - Non-Commercial Use Permitted
Crystal Structure Analysis and Trap Spectroscopy in Organic Semiconducting Crystals

A dissertation submitted to the
Swiss Federal Institute of Technology
Zurich

for the degree of
Doctor of Natural Sciences

presented by
Simon Haas
Dipl. Natw. ETH
born on May 5th 1974
citizen of Burgdorf BE - Switzerland

accepted on the recommendation of
Prof. Dr. B. Batlogg, examiner
Prof. Dr. T. Siegrist, co-examiner

2006
Preface

Today’s electronic industry mainly relies on silicon devices. Nearly perfect silicon wafers with charge carrier mobilities at room temperature in the range of 1000 cm²/Vs are the basis of fast integrated circuits. In order to save costs — and make the switching even faster — this high performance electronics is limited to small areas. For large area applications, such as display driver electronics, amorphous, hydrogenated silicon (a-Si:H) is used instead: With mobilities around 1 cm²/Vs, it is comparably slow, but still fast enough for low performance applications — at drastically reduced costs per area compared to crystalline Si. This field of low performance applications is where organic electronics will play an important role in future. With mobilities in the range of 1 cm²/Vs, organic materials can replace a-Si:H to some extent. As organic materials are processed at low temperatures compared to a-Si:H, cheap polymeric substrates can be used. If processed role-to-role by solution deposition (printing) on flexible substrates, circuits based on organic (semi)conductors will certainly set new standards for low production costs and minimize the investments. If organic materials can add an important feature, e.g. the mechanical flexibility, or show superior properties compared to their conventional, inorganic counterparts, they have a good chance to enter the market even faster. A good example are displays based on organic light-emitting diodes (OLEDs), which are bright, yet power-saving, and do not show the unpleasant viewing angle-dependence of conventional displays.

The physical key number of any electronic material is its charge carrier mobility $\mu$. Together with the channel length $L$ (which is limited by the fabrication process), the mobility gives the maximal switching speed $\nu \sim \mu/L^2$. Nevertheless, the mobility derived from polycrystalline organic thin-film devices is rather an extrinsic value dependent on the film morphology rather than an intrinsic material property. Moreover, contact and interface effects present in the devices additionally veil the material properties. Hence, organic single crystals, grown as perfect as possible, are explored in order to get an intrinsic mobility value for a certain material, serving as an upper boundary for thin-film devices planned for applications. However, single-crystal devices suffer from extrinsic factors, too, which has to be taken into account. Finally, detailed, deep knowledge of the charge transport (and
the physics at interfaces and contacts... in organic molecular crystals might substantially change the device development: from an — albeit successful — optimizing of the process parameters to a *systematic, specific* development.
Contents

Abstract ix

Zusammenfassung xiii

1 Introduction 1
   1.1 Motivation and Outline ................................................. 1
   1.2 Charge transport in OMCs .............................................. 3
   1.3 TD-SCLC ................................................................. 6

2 Experimental 11
   2.1 Materials ............................................................. 11
   2.2 Crystal Growth ......................................................... 13
   2.3 Characterization ....................................................... 14

3 Thermal Expansion, Libration and Translation in Tetracene, Pentacene and Rubrene 17
   3.1 Introduction ............................................................ 17
   3.2 Experimental ........................................................... 20
   3.3 Results and Discussion ................................................. 21
      3.3.1 Thermal Expansion in Acenes: Negative Thermal Expansion in Pentacene ........................................... 21
      3.3.2 Tetracene vs. Rubrene: The Influence of the Inertial Tensor on the Thermal Expansion ........................................... 28
   3.4 Conclusions ............................................................. 32
4 Metastable High Temperature Phase of Pentacene 35
   4.1 Introduction ...................................................... 35
   4.2 Results ............................................................ 37
   4.3 Conclusions ........................................................ 41

5 SCLC in Organic Single Crystals: Extracting the Trap DOS and Challenges in Reaching the Trap-Free Limit 43
   5.1 Introduction ...................................................... 43
   5.2 Experimental ..................................................... 45
   5.3 Results and Discussion ........................................... 47
      5.3.1 Influence of X-rays on the DOS ............................ 51
      5.3.2 Influence of oxygen to the DOS ............................ 53
   5.4 Conclusions ........................................................ 55

6 Electrical Properties of a New Rubrene Derivative 57
   6.1 Introduction ...................................................... 57
   6.2 Experimental Section ............................................. 58
   6.3 Results and Discussion ........................................... 59
      6.3.1 Structure ..................................................... 59
      6.3.2 Field-effect transistor measurements ....................... 61
      6.3.3 TD-SCLC measurements ..................................... 63
   6.4 Conclusions ........................................................ 66

7 Iodine Intercalation in Pentacene Thin Films and Single Crystals 67
   7.1 Introduction ...................................................... 67
   7.2 Experiment ........................................................ 69
   7.3 Results ............................................................. 70
      7.3.1 Structure ..................................................... 70
      7.3.2 Conductivity ................................................ 74
   7.4 Discussion ........................................................ 79
7.5 Conclusions ........................................... 81

8 Conclusions and Outlook  ................................... 83
Abstract

Several aspects of charge transport and structure in organic molecular crystals have been addressed in this thesis, including the density of trap states, chemical doping, the relation between molecular packing and hole mobility, thermal expansion and molecular motion.

Full structure characterizations by means of X-rays were carried out at various temperatures for tetracene, pentacene and rubrene. Together with thermal expansion and changes in the arrangement of the molecules, the temperature dependence of the molecular thermal motions reflects the anharmonicity of the molecular potential well. The thermal expansion in these van-der-Waals-bonded materials is of order $\alpha = 100 \times 10^{-6} \text{K}^{-1}$. The difference in anisotropy of the inertial tensors is reflected in the thermal expansion. While the expansion is highly anisotropic in the case of tetracene and pentacene with a large anisotropy in the inertial moments, it is more uniform and smaller in the more isotropic rubrene. With increasing number of benene rings, and thus increasing anisotropy of the molecular inertial tensor, the librations about and translations along the long molecular axis become the dominant feature in the acenes.

A particularity in the series of the acenes is the negative thermal expansion along $a$ in pentacene. The contraction along $a$ upon increasing temperature is mainly a result of the increasingly dominant librations about the long molecular axis and the decreasing herringbone angle, supported by the absence of larger librations and translations perpendicular to the long molecule axis due to steric hindrance.

Furthermore, we have determined the structure of a high-temperature polymorph of pentacene, which is stable above 478 K. Its structure is consistent with that reported initially in 1962 and that has not been reproduced since in bulk single crystals. The herringbone-type 2-dimensional layers are identical in both polymorphs, whereas their layer stacking strongly differs.

As a consequence of the large, anisotropic thermal expansion and (in pentacene) the occurrence of a phase transition below the usual growth temperature, the temperature gradients in crystal growth and subsequent measurements have to be reduced in order to min-
imize the thermo-mechanical stress. The metastability of the pentacene high-temperature polymorph, which is supposed to be identical to the “bulk phase” in thin films, will have to be taken into account for device reliability.

The density of bulk trap states (DOS) in the gap was derived by temperature-dependent SCLC spectroscopy. In highest quality pentacene and rubrene derivative single crystals the DOS is as low as $\sim 10^{16}$ cm$^{-3}$eV$^{-1}$ and $\sim 10^{15}$ cm$^{-3}$eV$^{-1}$, respectively, at 0.2–0.5 eV from the valence band edge. Furthermore, we observe the onset of an exponential band tail with $E_c \sim 20$ meV in the best samples. Overall, the bulk trap density in pentacene crystals is higher than in rubrene and its derivative, but several orders of magnitude smaller than the values reported for the surface of pentacene and rubrene crystals. Since the observed band tail states are narrow, we ascribe their origin to static and also to dynamic fluctuations of the structure, i.e. thermal motion of the molecules. By taking into account the large number of states in the narrow band tails, we showed that in an usual SCLC experiment it is very difficult to shift $E_F$ into the valence band and thus to actually reach the trap-free limit in a SCLC experiment.

Extended exposure to ionizing X-rays influences the DOS of very clean samples significantly. As there is no formation of energetically discrete trap levels as a sign for chemical defects, rather an over-all increase of the DOS by one order of magnitude below 0.3 eV, we suppose structural defects as the origin of the increased in-gap DOS. These defects could be caused by impurities (created by radiation-induced reactions) which do not act as hole traps.

By comparing rubrene with a derivative with two added t-butyl groups (5,11-BTBR), the influence of the crystal structure on the charge carrier mobility was investigated. The semiconducting polymorph 2 has been electrically characterized. Presumably having a similar crystal structure and in-plane arrangement of the molecules as in rubrene, 5,11-BTBR (2) has shown a comparably high in-plane field-effect mobility of up to 12 cm$^2$/Vs (on an OTS-treated SiO$_2$ gate insulator). Fitting into the present understanding of the relation between structure and mobility, the in-plane mobility in 5,11-BTBR in its other polymorphic form (1) is too low to be measured because the tetracene backbones are twice as far apart from each other compared with rubrene, and $\pi$-stacking of the backbones is absent.

Finally, we report on in situ structural and conductivity studies of iodine intercalation, in both pentacene thin films and single crystals. This enabled us to address the intercalation dynamics, staging issues, and the structural intercalation phase diagram. For iodine-doped pentacene, we find that both thin films and single crystals intercalate easily, and are only found in an effectively metallic stage-1 structure across the whole temperature--
iodine partial pressure phase diagram that was assessed. For pentacene thin films, we find that successive intercalation and desorption induces an irreversible and controlled change in the polymorph of the crystal structure. Intercalated single crystals also show a quasi-metallic behavior of the conductivity, although their structural degradation due to the iodine intercalation, as monitored by the width of the rocking curve, is much more pronounced compared to thin films.
Zusammenfassung

Im Rahmen dieser Dissertation wurden verschiedene Aspekte des Ladungstransportes und der Kristallstruktur in organischen Molekülkristallen untersucht, darunter die Defektzustandsdichte, chemisches Dotieren, der Zusammenhang zwischen der Anordnung der Moleküle im Kristall und der Löcherbeweglichkeit, die thermische Ausdehnung und die thermische Bewegung der Moleküle.

Kristallstrukturanalysen von Tetrazen, Pentazen und Rubren wurden bei mehreren Temperaturen durchgeführt. Zusammen mit der thermischen Ausdehnung und Änderungen in der Anordnung der Moleküle spiegelt die Temperaturabhängigkeit der thermischen Molekülbewegungen die Anharmonizität des Kristallpotentials wider. Die thermische Ausdehnung in diesen van-der-Waals-gebundenen Materialien ist rund $\alpha = 100 \times 10^{-6} \text{ K}^{-1}$. Die Unterschiede in der Anisotropie der molekularen Trägheitstensoren manifestieren sich in der thermischen Ausdehnung. So ist die thermische Ausdehnung äußerst anisotrop für Tetrazen und Pentazen, die beide ein stark anisotropes Trägheitsmoment besitzen, aber gleichmäßiger und geringer im isotropen Rubren. Mit der Anzahl Benzolringe steigt die Anisotropie des Trägheitsmoments. Als Folge entwickelt sich in den Azenen die Libration um die lange Molekülachse und die Translation entlang dieser Achse als dominierende thermische Bewegung.


Weiter haben wir die Struktur eines Hochtemperatur-Polymorphs von Pentazen bestimmt, welches über 478 K stabil ist. Die Struktur ist konsistent mit der 1962 ursprünglich für Pentazen bestimmten Struktur, die jedoch seitdem nicht mehr in Einkristallen reproduziert werden konnte. Die Herringbone-Anordnung innerhalb der molekularen Schichten ist identisch für beide Polymorphe; dagegen unterscheidet sich die Stapelung der Schichten...
beträchtlich.


Die Dichte der Defektzustände (DOS) in der Energieücke wurde durch temperaturabhängige SCLC-Spektroskopie bestimmt. Pentazen- und Rubrenderivat-Kristalle von höchster Qualität haben zwischen 0.2 und 0.5 eV Zustandsdichten im Bereich von \( \sim 10^{16} \text{cm}^{-3} \text{eV}^{-1} \) respektive \( \sim 10^{15} \text{cm}^{-3} \text{eV}^{-1} \). Weiter beobachten wir in den besten Proben den Anfang eines exponentiellen Bandtails mit \( E_c \sim 20 \text{meV} \). Generell ist die Defektdichte in Pentazenkristallen höher als in Rubren und dem Rubrenderivat, aber immer noch um Grössenordnungen tiefer als die publizierten Defektdichten an der Oberfläche von Pentazen- und Rubrenkristallen. Da die beobachteten Tailstates schmal sind, führen wir ihren Ursprung sowohl auf *statische*, als auch auf *dynamische* Strukturfektuationen zurück, also thermische Bewegung der Moleküle. Unter Berücksichtigung der vielen Zustände in den schmalen Bandtails haben wir gezeigt, dass es in konventionellen SCLC-Experimenten sehr schwierig sein dürfte, \( E_F \) bis ins Valenzband zu schieben und so das “trap-free limit” tatsächlich zu erreichen.

Längere Einwirkung von ionisierender Röntgenstrahlung verändert die DOS von sehr reinen Proben deutlich. Da keine Bildung von energetisch scharf definierten Defekten beobachtet wird, sondern ein allgemeiner Anstieg der DOS um eine Grössenordnung unterhalb von 0.3 eV, vermuten wir strukturelle Defekte als Ursache für die erhöhte DOS. Diese Defekte können durch Verunreinigungen verursacht sein, wie sie bei strahlungsinduzierten Reaktion auftreten, und die selber keinen Löcherdefekt darstellen.

Durch den Vergleich von Rubren mit einem Derivat mit zwei angehängten \( t \)-butyl-Gruppen (5,11-BTBR) wurde der Einfluss der Kristallstruktur auf die Ladungsträgerbeweglichkeit untersucht. Das halbleitende Polymorph 2 wurde elektrisch charakterisiert. Vermutlich hat es eine sehr ähnliche Kristallstruktur und Anordnung der Moleküle wie Rubren. 5,11-BTBR (2) zeigt denn auch eine vergleichbar hohe in-plane Feldeffektbeweglichkeit von bis zu 12 cm\(^2\)/Vs (auf einem OTS-behandelten SiO\(_2\) Gate-Dielektrikum). Zum vorherrschenden Verständnis des Zusammenhangs zwischen Struktur und Beweglichkeit passt, dass die Beweglichkeit in 5,11-BTBR in seiner anderen polymorphischen Form (1) ummessbar klein ist. Denn die Tetrazen-Gerüste sind dort doppelt so weit voneinander entfernt wie
in Rubren, und es gibt keine Stapelung der \( \pi \)-Orbitale.

Chapter 1

Introduction

1.1 Motivation and Outline

Charge transport in organic semiconductors is of both fundamental and commercial interest: In contrast to most inorganic materials, less is known about the mechanism of charge transport in organic materials. Phenomena like polaron formation, electron-electron interaction and electron-phonon coupling play an important role, and the validity of a single-electron band model is questionable [1, 2]. A broad range of different theories exists which still cannot explain the variety of experimental data, since additional factors like structural imperfections and trap states veil the intrinsic material properties. On the other hand, applications require reliable performance of each single device in order to enable integration of thousands of them to complex circuits. Lifetime is an important issue as well.

The mobility as the key performance criterion, both for applications and basic science, depends on several factors: A very basic one is the packing of the molecules in the crystal, because it defines the overlap of the molecular orbitals, which is most important for the intrinsic mobility. Apart from the static structure, the dynamics of the structure affects the transport due to fluctuations of the molecular overlap or scattering at phonons, as well as due to structural imperfections induced by thermal strain upon anisotropic thermal expansion. As a consequence, part of the charge carriers are trapped or scattered, and the effective mobility is decreased. Furthermore, the reliable extraction of the mobility is hampered by extrinsic effects that go with the measurements.

Therefore, this thesis illuminates properties of organic semiconductors by addressing the interplay between dynamic/static structure, density of trap states and charge transport. Charge transport basically consists of two steps: 1) charge carriers have to be introduced,
and 2) charge carriers move in the solid. In this thesis, introduction of charge into the organic semiconductor is realized by space-charge injection and chemical doping. Once injected, carriers are characterized by their mobility. Due to chemical and structural imperfections, charge carriers are scattered or trapped. Consequently, the density of trap states is addressed as an important factor. Furthermore, structural studies are performed to investigate the possible origin of some of the defects.

The outline of this thesis is as follows: Organic semiconductors and some of the important aspects concerning charge transport in these materials are introduced in chapter 1. In particular, the method of temperature-dependent space-charge limited current (TD-SCLC) spectroscopy is explained. Chapter 2 covers the experimental details, including crystal growth and part of the characterization. Chapter 3 then concentrates on temperature-dependent structural studies, including analysis of the molecular thermal motion and thermal expansion. Further, a high-temperature phase transition in pentacene is reported in chapter 4. Chapter 5 gives experimental details of our TD-SCLC measurements and addresses common caveats of SCLC measurements. Further, density of states for pentacene crystals are reported that confirm the high crystal quality. Finally, the influence of exposure to X-rays or oxygen on the DOS is discussed. The relation between crystal structure and mobility in a rubrene derivative is content of chapter 6. Then, chemical doping of pentacene by iodine intercalation is addressed in chapter 7. The thesis ends with the conclusions from the structural and electronic studies, and gives an outlook.
1.2 Charge Transport in Organic Semiconductors

Molecular solids differ from well-known covalently bonded inorganic materials like silicon or germanium in many ways: Due to only weak interactions between the molecules, the molecules preserve a lot of their electronic properties in the solid state, and the relevant energy bands are expected to be narrow (Δ ~1-500 meV, compared to several eV in Si, as depicted in Fig. 1.1). Therefore, phenomena like polaron formation, electron-electron interaction and electron-phonon coupling might become crucial, and the validity of a single-electron band model is questionable [1, 2].

Organic materials contain mainly carbon and hydrogen atoms, which are covalently bonded to neutral molecules. Common to the (semi)conducting organic molecules is that they contain delocalized π-electrons in extended conjugated or aromatic systems, which are built up from the atomic $p_z$-orbitals of carbon. Spatial proximity and a suitable orientation of these molecular π-orbitals in the crystal leads to π-π interaction (overlap). Since the molecules are held together in the condensed state by weak van-der-Waals (vdW) forces, the π-π overlap is small compared to covalent bonds and prohibits the easy formation of broad energy bands in organic semiconductors. Thus localized states (on the single molecules) are often favoured. As a consequence, one often observes hopping transport instead of band transport. Hopping also implies that phase coherence is lost. In a band picture, the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) $\pi/\pi^*$ level of the isolated molecules become the valence band and the conduction band, respectively, in the crystal. Therefore, the band gap is closely related to

Fig. 1.1: Band structures for silicon (taken from Ref. [3]) and pentacene, calculated in the tight-binding approximation (taken from Ref. [4]).
the energy difference between the HOMO and the LUMO level. In the solid, these energy levels are modified by the electronic polarization: An additional (n-type) or a missing (p-type) charge on a molecule is stabilized by the polarization of the surrounding molecules, which leads to an adiabatic band gap $E_{\text{ad}}$ considerably smaller than the optical band gap. Still, an energy gap of order one to several eV remains.

As a consequence, the intrinsic carrier concentration $n_i$ due to thermal excitation is very small, resulting in a highly insulating behavior. Therefore, additional charge has to be induced in order to measure charge transport in these materials, yielding fundamental properties such as the charge-carrier mobility $\mu$. Different methods can be used to analyze charge transport: Transport near/at the surface of the crystal is mainly investigated using a field-effect transistor (FET) geometry, whereas bulk transport is typically studied using time-of-flight (TOF) or space-charge limited current (SCLC) measurements.

Injection of charge carriers by field-effect creates a thin layer with an enhanced carrier concentration at/near the surface of the crystal, i.e. at the interface to the dielectric. By the applied gate voltage $V_G$, the carrier concentration can be adjusted in a wide range, as well as the carrier type (p or n) can be selected by the correct sign of $V_G$.

TOF is used relatively seldom with success due to experimental limitations, e.g. insufficient sample size and quality. In contrast to all other methods mentioned above, contact effects are excluded in TOF, since photogeneration of charge carriers happens within the sample.

On the other hand, although often used, SCLC is not an easy-to-use method without caveats (see chapter 5), e.g. partially blocking or limiting contacts instead of ohmic contacts are critical because they veil the intrinsic properties. As SCLC measurements are an important part of this thesis, the essential theory is discussed separately in the following section.

Sometimes, unintentional doping by chemical impurities slightly decreases the ohmic resistance. However, intentional chemical doping in organics differs strongly from “conventional” doping (e.g. P in Si), as the concentration of the dopant may even exceed the concentration of the host molecules, resulting in a new compound. As a consequence, the crystal structure is often drastically modified, causing changes in the orbital overlap and thus altering the band structure itself. Furthermore, an overall degradation of the crystal quality might be observed due to the structural transition (see chapter 7).

The mechanism of charge transport in organic molecular materials is still difficult to predict. Whether band-like or hopping transport occurs is usually determined by several

---

1Nevertheless, if applied with great expertise and suitable ultra high purity samples provided, TOF measurements can deliver truly intrinsic transport properties, e.g. the conductivity tensor for holes and electrons, as shown by N. Karl and coworkers for various materials (see ref. [5] and refs therein).
parameters: Small disorder and good overlap should lead to band transport (with \( \mu \propto \text{bandwidth} \)), small overlap and high disorder to hopping. Band-like and hopping transport can be distinguished from the temperature dependence of the mobility. For band-like transport, \( \mu \) increases with decreasing temperature due to reduced scattering at the phonons at lower temperature. In contrast, phonons are essential for the release of the localized charge carriers in any hopping model. Therefore, hopping transport is thermally activated, i.e. \( \mu \) decreases with decreasing temperature, albeit almost every non-band-like temperature dependence can be obtained with one of the many hopping models proposed.

Due to non-cubic crystal structures and the anisotropy of the intermolecular \( \pi \)-overlap, anisotropic transport properties are expected. Depending on the direction of transport and the carrier type, different charge transport mechanism can coexist. In naphthalene, band-like transport within the molecular layers was found for holes and electrons, while perpendicular to the layers, as a result of the small overlap, hopping transport for electrons gave the best fit \[6\].

Two models, which are particularly useful for the description of charge transport in organic molecular crystals shall be shortly introduced here. One is the (extended) Holstein-model \[8\] in which a temperature-dependent bandwidth \( W \) of the extended states due to electron-phonon-coupling is the basic idea. With strong electron-phonon-coupling, \( W \) is narrow (\( \leq 10 \text{meV} \)), and therefore the charge carriers are localized at room temperature, leading to hopping transport. Only at low temperature, \( W \) is as high as \( >100 \text{meV} \), resulting in band-like transport \[7\]. The second model is the standard transport model, which has been successfully used for amorphous silicon originally. In this model, both extended and localized states exist, separated by the mobility edge. Only charge carriers in extended (= band) states contribute to the current. Usually, the Fermi level is several \( kT \) away from the mobility edge (\( E = 0 \)), i.e. within the localized states. A small amount of charge carriers in these occupied localized states can thus be thermally activated into the extended states (Boltzmann statistics) and contribute to the current.
Another important point, which must not be neglected, is charge trapping. Because of changes in the local polarizability, chemical and structural defects lead to modified energy levels, resulting in active trap states within the energy gap or scattering centers (anti-traps) below the valence band edge $E_v$ and above the conduction band edge $E_c$, respectively. Depending on their energetic position in the gap, trap states can either specifically trap holes or electrons. In a typical organic device, defects can be divided into two categories: Interface/surface and bulk defects. Former include defects at the contact/semiconductor interface as well as trapping/scattering at the interface of a FET device. Bulk defects originate from structural disorder and stacking faults like vacancies, interstitials and twinning, and also from chemical impurities. If trapping is present, not all injected ($n_{\text{tot}}$) charge carriers are free ($n_{\text{free}}$), and only an effective mobility $\mu_{\text{eff}} = (n_{\text{free}}/n_{\text{tot}})\mu_0$ is measured. Thus, knowledge of the trap distribution finally enables the calculation of the intrinsic (band) mobility $\mu_0$. Basic measurements and analyses of current-voltage characteristics can already give a measure for the density of (deep) trap states; trapping is also visible in the hysteresis of FET characteristics. A more sophisticated evaluation of the $I$-$V$ characteristics in temperature-dependent SCLC experiments finally yields the density of trap states (DOS) in the gap as a function of energy, as explained in the following section. Other methods for extraction of the DOS include thermo-stimulated current (TSC), thermo-stimulated luminescence (TSL) and optical measurements.

Organic thin films are relatively easy to fabricate by thermal evaporation, spin coating or dropcasting, but consist usually of differently oriented crystallites with a large amount of grain boundaries or are amorphous. To overcome these extrinsic device limitations, single crystals are essential for studying the intrinsic (transport) properties of organic molecular materials. On the other hand, taking into account all kind of obstacles that are usually present, even in excellent organic samples — defects, contact effects — the measurements yield results on the device physics rather than intrinsic material physics in many cases for single crystals as well. Exploring new ways of the sample preparation and measurement setup in order to exclude extrinsic effects leading directly to intrinsic results is the only way out, which depends on the qualitative and quantitative investigation of the origin of the defects.

1.3 DOS spectroscopy: Temperature-Dependent Space-Charge Limited Current

In the space-charge limited current (SCLC) regime, the current between the contacts is not only due to the movement of the intrinsic (thermally activated) charge carriers by
the applied electric field, but additional charges are injected from the contacts. The original theory by Mott/Gurney [9] was derived for the trap-free insulator in a parallel-plate capacitor geometry (cf. Fig. 5.1a). In this case, the total injected charge $n_{\text{tot}}$ is given by [10]

$$n_{\text{tot}} = \frac{\varepsilon_r \varepsilon_0 U}{e L^2},$$  \hspace{1cm} (1.1)

where $\varepsilon_r$ stands for the dielectric constant of the insulator, $\varepsilon_0$ is the permittivity of vacuum, $U$ the applied voltage, $e$ the elementary charge and $L$ the spacing between the two electrodes. The current density $j$ is calculated from Ohm’s law and Poisson’s equation and results in Child’s law [10]:

$$j = \frac{9}{8} \mu_0 \varepsilon_r \varepsilon_0 U^2 L^3,$$  \hspace{1cm} (1.2)

with the intrinsic charge carrier mobility $\mu_0$. The dependence of the current (density) on $U^2$ is intuitive: The injected charge ($\propto U$) moves with velocity $v$, given by the applied electric field ($v \propto U$).

If bulk traps are present, the density of free carriers $n_f$ contributing to the current is reduced. Consequently, the current density decreases to

$$j = \frac{9}{8} \mu_0 \varepsilon_r \varepsilon_0 U^2 L^3 \theta,$$  \hspace{1cm} (1.3)

with the ratio $\theta = n_f/n_{\text{tot}} \leq 1$. In general, the ratio $\theta$ is not constant over the measurement range, leading to $I$-$V$ characteristics that are not easily interpreted. To simplify the evaluation, discrete trap levels or an exponential distribution are often assumed.

If the density of states (DOS) shows broad tail states, it is very difficult – if not impossible – to reach the trap-free limit (see chapter 6.4). On the other hand, a slope of 2 in the log($I$)-log($V$) plot, which is often interpreted as the trap-free regime according to Child’s law, can occur if the Fermi level enters the lower Gaussian tail [11]. This situation might often lead to a wrongly identified trap-filled limit. Thus the total trap density, estimated from the apparent trap-filled limit, often only covers the deep states, neglecting the very numerous band tail states. Extrinsic factors such as contact effects or an unsuitable cofacial measurement geometry strongly influence the interpretation, too. These aspects are further discussed in chapter 6.4

Going beyond basic SCLC analysis, temperature-dependent SCLC (TD-SCLC) spectroscopy allows the determination of an arbitrary shaped density of trap states (DOS). Only after knowing the DOS, an indisputable interpretation of a single (room temperature) SCLC curve is possible. TD-SCLC (or, originally, TM-SCLC [12, 13]) is a differential method, but the energy scale is determined separately from the experimental activation energies.

\footnote{An appropriate theory is still missing for a cofacial geometry of the contacts. Theory would have to take into account not only the non-uniform field distribution, but also consider the anisotropy of the mobility, resulting in a complicated charge/current distribution.}
For TD-SCLC, we assume the standard transport model (c.f. above). By injection of carriers, trap states become filled, and the Fermi energy is shifted towards the band edge \((E=0,\) see Fig. 1.3). The carriers contribute to the change in current due to thermal activation into extended states.

![Diagram showing the density of trap states and Fermi level](image)

The basic equations [12] are as follows: The trap states are filled due to the injected charge:

\[
n_{\text{tot}} = \int h(E) f(E, E_F, T) dE ,
\]

(1.4)

where \(h(E)\) stands for the density of (trap) states and \(f\) is the Fermi function. With increasing voltage, the Fermi level is shifted. Additionally injected charge is therefore given by

\[
\frac{d n_{\text{tot}}}{d E_F} = \int h(E) \frac{df(E, E_F, T)}{dE_F} dE .
\]

(1.5)

The connection to the measured \(I-V\) curve is given by:

\[
\frac{d n_{\text{tot}}}{d E_F} = \frac{1}{kT} \frac{\varepsilon U}{eL^2} \frac{2m-1}{m^2} (1 + C) ,
\]

(1.6)

with \(m = d \ln(j)/d \ln U\) and

\[
C = \frac{B(2m-1) + B^2(3m-2) + d \ln(1+B)/d \ln U}{1 + B(m-1)} .
\]

(1.7)

\(B\) contains higher order derivatives of \(j(U)\). The logarithmic slope \(m\) of the measured \(I-V\) curve thus contains the information about the density of states, \(h(E)\), which can be derived by deconvolution of eq. 1.5 with respect to \(df/dE_F\). This procedure works well for low enough temperatures as the derivative of \(f\) has to be a sharp peak. Apparently, \(h(E)\) could be reconstructed from one single curve, as it is done in purely differential SCLC, but a direct experimental measure for the energy is more reliable. This is done via the determination of the activation energy \(E_A\), which gives the approximate distance of \(E_F\) from the valence band edge (mobility edge) as function of the applied voltage:

\[
E_{\text{SCL}}^A = -\frac{d \ln(j(U))}{d (1/kT)} .
\]

(1.8)

An DOS-dependent correction has to be applied to get the dominant energy, where the
injected charge is centered:

\[ E_D = E_A^{SCL} + \frac{(3 - 4m)n}{(2m - 1)(m - 1)m} kT, \]  

(1.9)

where \( n = -\frac{dE_A/kT}{d\ln(U)} \).

Additionally, the effective mobility \( \mu_{\text{eff}} = (n_f/n_{\text{tot}})\mu_0 \) can be extracted directly from the experimental data:

\[ \mu_{\text{eff}} = \frac{j \varepsilon \varepsilon_0 L^3}{\varepsilon_r \varepsilon_0 U^2 (2m - 1)^2(m - 1)(1 + B)}, \]  

(1.10)

with the variables as defined above.

The theory of TD-SCLC relies on the following assumptions: (i) A sandwich-type sample with parallel electrodes, a homogeneous density of trap states \( h \), and a constant mobility \( \mu \) over the entire volume are considered, (ii) carriers (holes) are injected from an ohmic contact, (iii) diffusion of charge carriers can be neglected, and (iv) a quasi-equilibrium is reached at every measurement point. By definition, the energy scale is set to zero at the valence-band edge.
Chapter 2

Experimental

2.1 Materials

The following organic semiconductors were selected for the studies: tetracene (Tc), pentacene (Pc), rubrene (Ru), and a rubrene derivative (Ru5,11).

The materials were received from Fluka/Aldrich (Tc, Pc, Ru) or provided by Ciba SC (Ru5,11) as clean, microcrystalline powders. Since the given chemical purity of ~99% is not sufficient for studies of intrinsic electronic properties, some of the materials (Pc, Ru) were purified by vacuum sublimation in a temperature gradient prior to the crystal growth. Pentacene in particular was sublimed several (up to 5) times. To remove most

![Fig. 2.1: Left: Structural formulas of benzene and the linear acenes from naphthalene to pentacene, consisting of fused benzene rings. Right: Rubrene and 5,11-BTBR (t-butyl-tetraphenylrubrene), two derivatives of tetracene.](image-url)
of the inherent pentacene-quinone (“PcO₂”), at least one sublimation was carried out at lower temperature according to Ref. [14]. As-bought rubrene powder contained crystalline impurities or amounts of a different structural modification of rubrene, which could be removed by heating the powder to 260°C, as monitored by X-ray diffraction (XRD) in an in-situ experiment (see Fig. 2.2). Interestingly, these impurities present in rubrene powder are not identical with compound A or B reported by Zeis et al. [15]. After rubrene had been heated in a closed ampoule above the melting point, it did not recrystallize and consequently a phase transition to a glassy (amorphous) state was observed.

Fig. 2.2: Purification of rubrene powder by sublimation of the impurities, monitored in-situ by XRD. The pristine powder contains several peaks which cannot be attributed to rubrene, therefore indicating crystalline impurities, marked by black arrows. At 533 K, these additional peaks have disappeared. Consequently, the peaks measured after cooling down to room temperature correspond to pure rubrene. The peak positions are slightly shifted due to the temperature-dependent lattice constants. The measurement time was the same for all curves, which are displayed on the same scale and have been moderately smoothed. The bars indicate the theoretical positions of the reflections with a relative intensity >1%, calculated from the full structure at 298 K (cf. section 3.3.2).
2.2 Crystal Growth

Single crystals were grown by physical vapor transport (PVT)[16, 17], using high purity argon or hydrogen\(^1\) at atmospheric pressure as the transport gas or, alternatively, \textit{in vacuo}. A schematical (typical) temperature profile of a PVT furnace is shown in figure 2.3. Due to the temperature gradient and the resulting thermal convection and supported by the gas flow, PVT results in a spatial separation of the pure organic semiconductor material from “light” and “heavy” impurities (with lower and higher sublimation/crystallization temperatures, respectively). Thus, PVT results in a further chemical purification. The crystal growth tubes (pyrex or quartz glass) had a typical inner diameter of 1.4–2.0 cm, whereas the flow was adjusted to rates of 7–20 ml/min. For better handling, an additional inner glass tube served as a reservoir for the source material, and inner aluminum and glass shells were placed in the crystal growth zone. Since very thin crystals (≤3 µm) would easily stick irreversibly onto the glass due to electrostatic adhesion if accidentally tipped over, the yield could be increased by deployment of the metal shells — despite the thermal conduction by the metal which locally alters the temperature gradient. Prior to the crystal growth, the glass and aluminum parts were cleaned in aceton and ethanol and thoroughly rinsed with deionized water, and finally annealed at 350–450°C in a flow of pure hydrogen for several hours. The temperature as well as the growth and annealing

\(^1\)Initially, hydrogen was used as the transport gas, partially leading to the formation of pentacene-dihydride (PcH\(_2\)), which can be distinguished from pentacene by its different, reddish color.
periods were controlled by an Eurotherm 2416 programmable controller, and adjusted according to the desired crystal size. That is, very thin crystals for SCLC measurements (cf. section 5), thicker, larger crystals for iodine intercalation experiments (section 7) and bulky crystals for single crystal crystallography (sections 3 and 4). Under the conditions of PVT, all the studied materials preferentially showed a platelet or needle like habit with the large face \{001\} (for Ru, depending on the space group setting, also: \{100\}).

For some of the XRD studies (sections 3 and 4), pentacene crystals were grown \textit{in vacuo} in a closed glass ampoule, showing a bulky habit and developed faces other than \{001\}. Due to the low pressure, the growth temperature was reduced by 20–50°C compared to PVT at 1 atm. Since a two-zone furnace was used, the temperature profile was slightly different. Besides the benefit of a more suitable sample shape for single crystal crystallography, crystal growth \textit{in vacuo} also addresses another important issue: Large anisotropic thermal expansion coefficients (cf. section 3) are the reason for large stress/strain fields induced into the crystals upon cooling to room temperature after crystal growth. This stress/strain affecting the crystal quality can be reduced by a lower growth temperature, as realized \textit{in vacuo}, and by a slower cooling rate.

### 2.3 Characterization

The crystals were mainly characterized by XRD and transport measurements, described in more details in sections 3.2, 5.2 and 7.2.

Prior to the sample preparation and the measurements, all crystals were inspected under the stereo microscope (6.3–40x), as a homogeneous optical appearance serves as a first indication of reasonably good crystal quality. By inspection with crossed polarizers and transmitted light, transparent crystals could be checked whether they are single-domained. Multiple domains or twinning are revealed by the absence of complete extinction, which would be expected from the birefringent properties of the crystals. Since pentacene is transparent in visible light only up to a few microns thickness, optical inspection of thicker crystals was limited to their surfaces, which should be well developed and smooth. Apparently misoriented or cracked crystal parts were cut off.

Whereas most full structure determination work (chapter 3) was carried out using infrastructure at Bell Laboratories (USA), a STOE STADI P powder diffractometer served as an in-house multipurpose tool, covering powder diffraction and examinations of the \(d\)-spacings (\(\theta/2\theta\)-scan) and rocking curves (\(\omega\)-scan) of single crystal and thin film samples. The diffractometer is equiped with a CuK\(_{\alpha 1}\) source (convergent, focusing beam geometry) and a position sensitive detector (PSD), simultaneously collecting the diffracted intensi-
ties over a range of $6^\circ$. Two sample holders for powder measurements were available: a standard transmission sample holder, where a layer of powder, mixed with vacuum grease, is applied onto a thin polyacetylene foil, and a Debye-Scherrer sample holder, where the powder is positioned in a rotating low-absorbing glass capillary. With the latter, measurements at variable temperature in the range from room temperature to $260^\circ$C could be performed with a home-built heater, using a pre-heated stream of nitrogen gas flowing over the sealed capillary. Depending on the experiment, the materials were used as a powder as bought or ground up from (cleaner) crystals. As the materials are relatively soft and tend to form platelets due to their structural anisotropy, it is difficult to get a uniform powder. Additionally, the grinding process may induce stress/strain into the crystallites, leading to line broadening.

Since the diffractometer is originally designed for powder measurements only, one has to be careful when measuring and interpreting thin film and single crystal data. While the chosen step-size $\Delta \omega$ and the definition of $\omega_0$ are irrelevant for powder measurements, they strongly influence the intensities in $\theta/2\theta$ scans and their ratios for oriented samples. This can be understood by considering the influence of the rocking curve width\textsuperscript{2}: For high quality crystals with a rocking width smaller than the step in $\omega$ during a $\theta=\omega/2\theta$-scan, the integrated intensity for a reflection depends on the incidental position on the rocking curve, given by the fixed position $\omega$ of the sample during the integration interval. Figure 2.5 depicts a drastic example of “intensity tuning” by a small change of $\omega_0$ during the sample adjustment.

\textsuperscript{2}With the detector placed at the $2\theta$-position of a chosen reflection, the intensity $I$ is recorded as a function of the sample position ($\omega$), resulting in the so-called rocking curve. The width of $I(\omega)$ reflects the mosaic spread of the sample. Because the PSD resolves the position in $2\theta$, intensities measured at a certain $\omega$ have to be integrated over the full peak width in $2\theta$ (a few $1/10^\circ$). These integrated intensities versus $\omega$ correspond to the “classic” rocking curve experiment with a fully opened, stationary point detector, which covers a few $1/10^\circ$. Tiny crystals, much smaller than the broad, non-parallel X-ray beam of the STADI P diffractometer, allowed us to measure rocking curves as narrow as 0.03$^\circ$ FWHM (for Si 400). However, these values should not be taken as absolute values due to the limitations of the diffractometer, but it is still reasonable and instructive to compare them for e.g. two phases in the same sample (see chapter 7).
Fig. 2.5: Variation of the XRD intensities for a high quality (pentacene) single crystal: The stepsize ($\Delta \omega = 1^\circ$) and the integration time were the same for both $\theta/2\theta$-scans. Only by the adjustment of $\omega_0$, the ratio of the intensities of the 001 and 002 reflection is completely changed as a consequence of the non-continuous scan method, which is sensitive to the incidental position on the rocking curve of every individual reflection during intensity integration. Inset: Schematic rocking curve for 001 and 002 with indication of the sample positions $\omega$ during the integration periods.
Chapter 3

Thermal Expansion, Libration and Translation in Tetracene, Pentacene and Rubrene

In this chapter, thermal expansion and molecular motions in organic materials, in particular linear, unsubstituted acenes and rubrene, are addressed, together with implications on the crystal quality. After a short description of the structures, the dependence of the thermal expansion on the molecular inertial momentum and on the anisotropic molecular potential well are discussed. An interesting particularity is uniaxial negative thermal expansion which is found in pentacene.

3.1 Introduction

The interplay of the attractive (van-der-Waals) and the repulsive (Pauli exclusion) interaction between the molecules determines the way an organic material crystallizes. While v-d-W forces prefer the molecules to arrange parallel, the repulsive forces try to minimize the interaction by a perpendicular arrangement of the molecules. Often, a herringbone type structure is formed as a compromise, still resulting in a dense packing.

In the series of the linear, unsubstituted acenes, naphthalene [18, 19] and anthracene [20] are monoclinic with similar unit cell geometries, while tetracene [21] and pentacene\(^1\) [22, 23, 24] are both triclinic, but with different unit cell topologies (cf. Tab. 3.2 and 3.6). However, the molecular packing of the acenes is remarkably similar in all the systems, with herringbone packing of the molecules in 2-dimensional layers (see Fig. 3.1a) and a herring-

\(^1\)Polymorphism in pentacene is addressed in chapter 4.
bone angle of 51–52° at room temperature (cf. Fig. 3.6). Due to the \( sp^2 \)-hybridization of the carbon atoms, the molecules are flat (maximal deviation from the least squares plane below 0.016 Å e.g. in tetracene). Tetracene and pentacene show parallel alignment (\( \Delta<1^\circ \)) of the long molecule axes, but not naphthalene and anthracene. Rubrene [25, 26] is an exception; the crystal structure has a rather high orthorhombic symmetry, and the molecular packing adopts a slip-stack arrangement in 2-dim layers (Fig. 3.1b).\(^2\)

\(^2\)Bulgarovskaya et al. [25] use a different space group setting (\( Bbam \)) than e.g. Sundar et al. [27] and Goldmann et al. [28] (\( Acam \)), resulting in the interchange of \( a \) and \( b \). In this chapter, we use the “recommended” setting, \( Cmca \), which is also true for reference [26]. In \( Cmca \), the \( bc \)-plane corresponds to the extended crystal surface which is easily accessible to FET measurements (instead of the \( ab \)-plane).

---

Fig. 3.1: Ortep-3 drawings [29] of tetracene (a) and rubrene (b), highlighting the differences between the layered herringbone structure (naphthalene, anthracene, tetracene and pentacene) and the slip-stack packing found in rubrene. For clarity, only one layer of molecules is drawn with respect to the plane of the paper, and the hydrogen atoms are omitted in rubrene.
Thermal expansion in van der Waals bonded organic systems can have substantial values due to the rather weak intermolecular bonding strengths. For instance, the (linear) thermal expansion coefficient of silicon is about $3 \times 10^{-6} \text{K}^{-1}$, for amorphous SiO$_2$ $0.55 \times 10^{-6} \text{K}^{-1}$, but for polyvinyl $70–100 \times 10^{-6} \text{K}^{-1}$. Furthermore, organic materials are mechanically soft, and one observes, compared to inorganic materials, a low melting point and a high vapor pressure. Additionally, the thermal expansion is anisotropic in most organic materials due to non-cubic, often low symmetry. As a consequence, stress/strain fields may be induced and lead to crack formation, deformation, and even to pressure induced phase transitions [30]. Furthermore, they also affect temperature-dependent measurements by mechanical instability, and additionally, they may induce the formation of defects such as small angle grain boundaries that act as trap states.

Thermal expansion in molecular solids is chiefly governed by the anharmonicity of the molecular potential and not by the small temperature dependence of the intramolecular bonding distances. Since the vdW-bonding in molecular solids is anisotropic, slight changes in the molecular packing, for instance the relative position of molecules, are therefore expected to reflect the anharmonicity of the system. Furthermore, the description of thermal motion of the molecules by librational and translational motions of a rigid molecule (neglecting intramolecular modes) uses a harmonic approximation. Therefore, the temperature dependence of the librations and translations may also serve as an indication of the anharmonic nature of the molecular potential well, together with the thermal expansion and the change in molecular packing, e.g. the herringbone angle in the acenes.

Since the crystallographic symmetry for all the acenes is lower than orthorhombic, the main axes of the thermal expansion tensor are not aligned with the unit cell axes and have to be determined following the procedure described previously [31, 32]. In the case of monoclinic symmetry, at least one axis is parallel to the crystallographically unique $b$-axis, and for orthorhombic symmetry (e.g. rubrene), the main axes are aligned with the unit cell axes. The effect of the anisotropic thermal expansion may be visualized by considering a sphere of the material, which, upon temperature change, deforms into an ellipsoid (cf. Fig. 3.2).

An additional factor determining thermal expansion is the molecular inertial tensor, which, in the acene series, becomes more anisotropic with increasing number of benzene rings.

<table>
<thead>
<tr>
<th></th>
<th>$I_1$</th>
<th>$I_2$</th>
<th>$I_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubrene</td>
<td>3369</td>
<td>6042</td>
<td>8611</td>
</tr>
<tr>
<td>Tetracene</td>
<td>250</td>
<td>2151</td>
<td>2402</td>
</tr>
</tbody>
</table>

Table 3.1: Main inertial momentum, given in uÅ$^2$ for room temperature. In the case of tetracene, the average values of the two almost identical molecules in the unit cell are listed ($\Delta I/\langle I \rangle < 0.2\%$).
with the largest anisotropy so far for pentacene. In rubrene, the addition of four phenyl groups to the tetracene backbone reduces the anisotropy in the inertial tensor considerably (Table 3.1). Since librations are dependent on the respective inertial momentum, the thermal expansion is expected to reflect the anisotropy of the molecular inertial tensor.

While either overall \( (dV/dT < 0) \) or uniaxial \( (dl/dT < 0) \) negative thermal expansion (NTE) [33] has been observed in many inorganic compounds with \( \text{ZrW}_2\text{O}_8 \) [34, 35] as a prominent example of isotropic NTE over a large temperature range, only few (uniaxial) examples for organic systems are known so far (see Ref. [36] and refs. therein). For applications, substances showing NTE are of great interest since they allow for designing material mixtures with negligible thermal expansion, helping to overcome thermal stress/strain issues. Interestingly, we found a distinct uniaxial contraction in pentacene upon increasing temperature. Since the molecular packing is very similar in the series of acenes, NTE in pentacene is an exception which has to be explained. At all, NTE is non-trivial considering that the simple concept of anharmonic intermolecular potentials always leads to (positive) expansion to first order.

### 3.2 Experimental

Single crystals of tetracene, pentacene and rubrene were grown by physical vapor phase transport (PVT) [17] or \textit{in vacuo} (pentacene), as described in section 2.2.

![Fig. 3.2: Thermal expansion: Principal axes 1 and 2 versus the crystal axes \(a\) and \(b\) (schematic).](image)

Structural characterization at various temperatures was done by means of X-rays. Tetracene crystals were investigated between 106K and 295K, rubrene between 106K and 400K, using a conventional CCD equipped diffractometer (Oxford Diffraction Xcalibur 2, MoK\(\alpha\), with Cryojet temperature control system). Pentacene crystals were measured between 295K and 400K, using an ENRAF/Nonius CAD4 diffractometer (CuK\(\alpha\)) with a home-built temperature control system, and additionally between 120K and 413K, using the Swiss-Norwegian Beamline (SNBL, \(\lambda = 0.71\) Å) at ESRF (Grenoble). Crystallographic data for naphthalene and anthracene were taken from the literature [18, 19, 20].

Thermal expansion was calculated from the change of the lattice constants with temperature. As the various acenes crystallize in different, non-orthogonal structures, a direct comparison of the corresponding unit cell parameters is of limited value. More appropriate
3.3. RESULTS AND DISCUSSION

is a transformation of the thermal expansion along the crystal axes (\(\alpha_i\)) into an orthogonal reference system, yielding the direction and the magnitude of the thermal expansion ellipsoid main axes \(\alpha'_i\) (principal axes, eigenvalues of the thermal expansion tensor), as schematically depicted in Fig. 3.2. We used the program STRAIN. It basically transforms the unit cells at two given temperatures into an orthogonal coordinate system, in which the thermal expansion is calculated and transformed into its main axes. Details of the procedure are described in Refs. [31] und [32]. The FORTRAN source code [32] was modified to explicitly display the transformation matrices and the components of the eigenvectors.

Libration and translation values for a rigid molecule motion (TLS analysis [37]) were extracted from the refined individual atomic anisotropic thermal parameters, using PLATON [38]. Care has to be taken that a sufficiently large area of reciprocal space is included for the thermal parameters to be well defined.\(^3\) An orthogonal coordinate system is given by the main axes \(I_i\) of the molecular inertial tensor(s), see Fig. 3.8 for an example. Main librations and translations are not necessarily in line with the molecular inertial system, since they may be mixed (coupling “S”). Mixing is thus expressed by non-zero out-of-diagonal elements of the respective tensors. Hence, the angles between \(L_i\) \(T_i\) and \(I_i\) can be calculated. Data for naphthalene and anthracene from the literature [18, 19, 20] were used for comparison.

3.3 Results and Discussion

3.3.1 Thermal Expansion in Acenes: Negative Thermal Expansion in Pentacene

The unit cell parameters for pentacene single crystals at different temperatures are given in table 3.2. Full structure data are available from the CCDC with ref.no. XXXXXX.

A plot of the change of the unit cell axes in pentacene reveals a negative thermal expansion coefficient \(\alpha_a\) along \(a\) (Fig. 3.3). This has been already observed by Mattheus et al. [39] from powder measurements, although the NTE along \(a\) is inconsistent with their single crystal structure obtained at 90 K [24], which, on comparison with the structure at room temperature, indicated a positive thermal expansion along \(a\), too. For comparison to other acenes, the thermal expansion coefficients are expressed in orthogonal principal axes (eigenvalues of the thermal expansion tensor). These eigenvalues \(\alpha'_i\) are plotted in Fig. 3.4 for three pentacene samples, measured with different setups. The trend for naph-

\(^3\)Consequently, data collection has to be performed up to high enough angles/indices, a task which is not easily fulfilled with Cu radiation due to the longer wavelength \(\lambda=1.54\) Å, compared to 0.71 Å for Mo.
Chapter 3. THERMAL EXPANSION IN TC, PC AND RU

Fig. 3.3: Temperature dependence of the lattice constants of pentacene (single crystal, CuK\_\(\alpha\)-data, simple temperature control). Expansion in the ab-plane is strongly anisotropic and negative in a-direction. (This data corresponds to the open symbols in Fig. 3.4.)

Table 3.2: Lattice parameters for pentacene for various temperatures. The unit cell axes are given in Å, the angles in deg, and the volume in Å\(^3\).

<table>
<thead>
<tr>
<th></th>
<th>Pentacene ((\lambda=1.54) Å)</th>
<th>Pentacene(^a) ((\lambda=0.71) Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>295 K</td>
<td>383 K</td>
</tr>
<tr>
<td>(a)</td>
<td>6.265(2)</td>
<td>6.212(1)</td>
</tr>
<tr>
<td>(b)</td>
<td>7.777(2)</td>
<td>7.881(1)</td>
</tr>
<tr>
<td>(c)</td>
<td>14.536(4)</td>
<td>14.657(2)</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>76.48(2)</td>
<td>75.96(1)</td>
</tr>
<tr>
<td>(\beta)</td>
<td>87.67(2)</td>
<td>86.56(1)</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>84.71(2)</td>
<td>84.86(1)</td>
</tr>
<tr>
<td>(V)</td>
<td>685.5(3)</td>
<td>692.78(17)</td>
</tr>
</tbody>
</table>

\(^a\)The lattice constants derived from the measurements at the SNBL using an area detector have been corrected (by 0.32 %) according to the unit cell determination with a conventional CAD4 diffractometer, giving higher precision absolute unit cell values when the reflections are chosen intelligently and measured at ±2\(\theta\) and different orientations of the crystal to cancel misalignment effects.

Thalene, anthracene and tetracene indicates a dependence of the largest thermal expansion coefficient on the length of the acene molecule. There is at least one direction with a value close to zero in all three. In contrast, pentacene has a direction with negative thermal expansion, as well as a much larger intermediate and maximum positive thermal expansion coefficient.
3.3. RESULTS AND DISCUSSION

Fig. 3.4: The eigenvalues of the expansion tensor ($\alpha'_i$) for acenes with $n=2, 3, 4,$ and 5 benzene rings. The eigenvectors are not parallel to the crystal axes (besides one direction along the $b$ axis in the monoclinic systems.) Data for naphthalene taken from Oddershede et al. [19] and Brock et al. [18](light symbols), and for anthracene from Brock et al. [20]. The three datasets for pentacene were obtained from different setups: CuK$_\alpha$ with point detector (■), CuK$_\alpha$ with point detector and preliminary temperature control (□) and synchrotron data (CCD, light symbols).

Table 3.3: The eigenvalues $\alpha'_i$ [$10^{-6}K^{-1}$] (main axes of the thermal expansion ellipsoid) after transformation to an orthogonal system. The volume expansion coefficient $\gamma$ is given as $\sum \alpha'_i$, or is derived directly from the experimental volume change, respectively. The density $\rho$ [g/cm$^3$] is given for room temperature.

<table>
<thead>
<tr>
<th></th>
<th>Naphthalene$^a$</th>
<th>Anthracene$^b$</th>
<th>Tetracene$^c$</th>
<th>Pentacene$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha'_1$</td>
<td>206(8)</td>
<td>127(2)</td>
<td>100.2(8)</td>
<td>123(4)</td>
</tr>
<tr>
<td>$\alpha'_2$</td>
<td>39(2)</td>
<td>32(1)</td>
<td>32(1)</td>
<td>75(5)</td>
</tr>
<tr>
<td>$\alpha'_3$</td>
<td>6(4)</td>
<td>21(1)</td>
<td>6.0(8)</td>
<td>-31(6)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>251(9)</td>
<td>181(3)</td>
<td>138(2)</td>
<td>167(8)</td>
</tr>
<tr>
<td>$\gamma_{\text{exp}}$ $^e$</td>
<td>240</td>
<td>175</td>
<td>136</td>
<td>168</td>
</tr>
<tr>
<td>$\rho$</td>
<td>1.214</td>
<td>1.251</td>
<td>1.305</td>
<td>1.349</td>
</tr>
</tbody>
</table>

$^a$Based on the lattice constants at 92 K and 296 K from Ref. [18].
$^b$Based on the lattice constants at 94 K and 295 K from Ref. [20].
$^c$Based on the lattice constants at 106 K and 295 K.
$^d$Based on the lattice constants at 295 K and 383 K; CuK$_\alpha$ ($\lambda=1.54 \text{ Å}$).
$^e$Directly calculated from the measured volume change, with room temperature volume as reference.
In the context of the series, this is an anomalous behavior, which is also expressed by the large volume expansion of pentacene. The dispersion of the values derived with different setups is inevitable, especially if comparing data obtained by area detection (CCD) with that by point detectors \(^4\).

Fig. 3.5 shows the direction of the main axes of the thermal expansion ellipsoid with respect to the pentacene molecules and the unit cell. The direction of most pronounced NTE (axis 3) encloses an angle of 22° with the crystallographic axis \(a\) and is nearly perpendicular to the crystallographic axes \(b\) and \(c\). The direction of maximal expansion (axis 1) encloses an angle of 26° with \(b\) and 50° with \(c\), being almost perpendicular to \(a\). The anomalously large intermediate eigenvalue (axis 2) corresponds to an out-of-plane direction, but is not exactly parallel to the long molecular axis.

To explain the negative thermal expansion in pentacene, we consider the temperature dependence of the thermal motions and the orientation of the molecules (herringbone/tilt angle, definitions see Fig. 3.5).

---

\(^4\)Unit cell dimensions determined with area detector data tend to have very small error bars due to the statistics involving up to several 1000 reflections, which are used for the least-squares refinement. However, for absolute values, a well adjusted “conventional” system, equipped with a point detector, is often the better choice [40].

Fig. 3.5: Thermal expansion in pentacene: The main axes of the thermal expansion ellipsoid are non-parallel to all crystal axes. Axis 3 (eigenvector to the value of minimal expansion) corresponds to a negative expansion, i.e. contraction in that direction nearly parallel to \(a\), whereas maximum expansion directs about along \(b\) and towards the center molecule (axis 1). For numerical values, see Fig. 3.4. \(\theta\) is the herringbone angle, and \(\delta\) the tilt angle, as referred in the text.
The libration and translation values for the rigid molecule motion are listed in table 3.4. The longer acene molecules show the expected increase in the anisotropy of the molecular inertial tensor. Whereas the inertial momentum about the long molecular axis, $I_1$, increases linearly with the number $n$ of benzene rings, $I_2$ and $I_3$ grow quadratically with $n$, because the distance $r_i$ of the (C) atoms from the axis goes in as $r^2$. The longer the molecule the smaller are the librations and the more does $L_{11}$ coincide with the molecular inertial system. Considering the off-diagonal elements of the libration tensor, $L_{11}$ describes a movement independent from $L_{22/33}$ and aligned with $I_1$ only in the case of pentacene (misalignment $< 5^\circ$) and tetracene ($<7^\circ$). Meanwhile, the translations stay almost constant with increasing number ($n$) of benzene rings, with a small increase from naphthalene to tetracene, and a decrease for pentacene again.

Interestingly, the values for the herringbone angle $\theta$ (see Fig. 3.5) are close for all acenes,

Table 3.4: Translation and libration parameters for linear acenes at room temperature. Libration parameters $L_{ii}$ are in deg$^2$, translation parameters $T_i$ in $10^{-2}$ Å$^2$. For the monoclinic acenes, the two molecules in the unit cell are crystallographically identical. In case of triclinic symmetry, they are independent, creating additional parameters $L'_{ii}$ and $T'_i$ for the second molecule. The main axes of the inertial tensor, $I_i$, are given in Å$^2$ amu, and also normalized with the number $n$ of benzene rings. $I_1$ (smallest momentum) points along the long molecular axis. $n$ is the number of benzene rings.

<table>
<thead>
<tr>
<th>$(n)$</th>
<th>Naph$^a$ (2)</th>
<th>Ac$^b$ (3)</th>
<th>Tc (4)</th>
<th>Pc (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetry</td>
<td>mono</td>
<td>mono</td>
<td>tri</td>
<td>tri</td>
</tr>
<tr>
<td>$I_1$ $(\div n)$</td>
<td>130 (65)</td>
<td>189 (63)</td>
<td>250 (62)</td>
<td>311 (62)</td>
</tr>
<tr>
<td>$I_2$ $(\div n)$</td>
<td>356 (178)</td>
<td>1001 (334)</td>
<td>2151 (538)</td>
<td>3957 (791)</td>
</tr>
<tr>
<td>$I_3$ $(\div n)$</td>
<td>486 (243)</td>
<td>1190 (397)</td>
<td>2402 (601)</td>
<td>4268 (854)</td>
</tr>
<tr>
<td>$L_{11}$</td>
<td>19.32</td>
<td>15.3</td>
<td>11.07</td>
<td>9.55</td>
</tr>
<tr>
<td>$L_{22}$</td>
<td>12.18</td>
<td>7.2</td>
<td>4.51</td>
<td>2.69</td>
</tr>
<tr>
<td>$L_{33}$</td>
<td>16.55</td>
<td>10.3</td>
<td>3.71</td>
<td>2.17</td>
</tr>
<tr>
<td>$L'_{11}$</td>
<td>13.01</td>
<td>9.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$L'_{22}$</td>
<td>5.25</td>
<td>2.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$L'_{33}$</td>
<td>4.19</td>
<td>2.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T_1$</td>
<td>3.18</td>
<td>4.77</td>
<td>5.461</td>
<td>4.240</td>
</tr>
<tr>
<td>$T_2$</td>
<td>2.37</td>
<td>3.02</td>
<td>2.991</td>
<td>2.288</td>
</tr>
<tr>
<td>$T_3$</td>
<td>1.58</td>
<td>1.94</td>
<td>2.632</td>
<td>2.205</td>
</tr>
<tr>
<td>$T'_1$</td>
<td>4.636</td>
<td>4.504</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T'_2$</td>
<td>2.876</td>
<td>2.408</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$T'_3$</td>
<td>2.646</td>
<td>2.069</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Values from Ref. [18].
$^b$Values from Ref. [20].
irrespective of the symmetry of the unit cell, and show the same qualitative temperature dependence (see fig. 3.6).

By the change of the herringbone angle and the increasingly dominant librations $L_{11}$ about the long molecular axis, a distinctly anisotropic expansion in the $ab$-plane is expected, as sketched in Fig. 3.7: The librating molecules at the corners of the unit cell interact with the one in the center, trying to keep a minimal distance also with larger librations at higher temperatures. The longer the molecule is, and thus the smaller the (relative) shift of the molecules, the larger is the repulsive interaction of the $\pi$-electron systems. With a relative “non-interacting” shift $d_{\text{b}}^b=0.19$ (about one benzene ring out of five), the interaction along $b$ is enhanced in pentacene compared to tetracene ($d_{\text{b}}^b=0.24$, one out of four), leading to a larger expansion along $b$. It should be noted that this simplified picture of one dominant libration $L_{11}$ is only valid for pentacene and tetracene, where the inertial tensor is anisotropic enough to align $L_{11}$ with the long molecular axis within $5$–$7^\circ$, but not for the shorter acenes. The further increased ratio $L_{11}/L_{22,33}$ in pentacene compared to tetracene is critical for the contraction along $a$, together with the slightly

Fig. 3.6: Temperature-dependence of the herringbone packing: The angle between the two molecules in the unit cell ($\theta$) is in the same range for all acenes. The temperature dependence is stronger for naphthalene and anthracene, and very similar, but weaker for tetracene and pentacene. Data for naphthalene taken from Oddershede et al. [19] and Brock et al. [18](light symbols), and for anthracene from Brock et al. [20]. For pentacene with CuK$_\alpha$ (full symbols) and synchrotron data (light symbols).
3.3. RESULTS AND DISCUSSION

Table 3.5: Translation and libration parameters for pentacene (single crystal, synchrotron data with \( \lambda = 0.71 \text{Å} \), and tetracene. Libration parameters \( L_{ii} \) are in deg\(^2\), translation parameters \( T_i \) in Å\(^2\). Due to triclinic symmetry, the two molecules in the unit cell are independent, creating additional parameters \( L'_{ii} \) and \( T'_{i} \) for the second molecule.

<table>
<thead>
<tr>
<th></th>
<th>Pentacene</th>
<th>Tetracene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>120 K</td>
<td>293 K</td>
</tr>
<tr>
<td>( L_{11} )</td>
<td>3.89</td>
<td>9.55</td>
</tr>
<tr>
<td>( L_{22} )</td>
<td>0.88</td>
<td>2.69</td>
</tr>
<tr>
<td>( L_{33} )</td>
<td>0.83</td>
<td>2.17</td>
</tr>
<tr>
<td>( L'_{11} )</td>
<td>3.65</td>
<td>9.59</td>
</tr>
<tr>
<td>( L'_{22} )</td>
<td>1.02</td>
<td>2.76</td>
</tr>
<tr>
<td>( L'_{33} )</td>
<td>0.65</td>
<td>2.06</td>
</tr>
<tr>
<td>( T_1 )</td>
<td>0.02011</td>
<td>0.04240</td>
</tr>
<tr>
<td>( T_2 )</td>
<td>0.01282</td>
<td>0.02288</td>
</tr>
<tr>
<td>( T_3 )</td>
<td>0.01059</td>
<td>0.02205</td>
</tr>
<tr>
<td>( T'_{11} )</td>
<td>0.02154</td>
<td>0.04504</td>
</tr>
<tr>
<td>( T'_{22} )</td>
<td>0.01262</td>
<td>0.02408</td>
</tr>
<tr>
<td>( T'_{33} )</td>
<td>0.01046</td>
<td>0.02069</td>
</tr>
<tr>
<td>( \theta^a )</td>
<td>51.63</td>
<td>52.11</td>
</tr>
<tr>
<td>( \delta_{\text{Mol.1}}^b )</td>
<td>25.79</td>
<td>25.10</td>
</tr>
<tr>
<td>( \delta_{\text{Mol.2}} )</td>
<td>24.99</td>
<td>24.26</td>
</tr>
</tbody>
</table>

\(^a\)Herringbone angle, derived from the two least square planes through all C atoms of each molecule.
\(^b\)Tilt angle: angle between the long molecular axis and \( c^* \).

smaller (temperature-dependence of the) translational motions \( T_{2,3} \). Thus there is less tendency of expansion in pentacene which could compensate the contraction, as it is the case in tetracene. An additional factor for the negative expansion is found in the increased vdW forces along \( a \) due to an decreased shift of the pentacene molecules: The tilt angle \( \delta \) against \( c^* \) (definition in Fig. 3.5) is decreased from \( \bar{\delta}=25.4^\circ \) at 120 K over \( \bar{\delta}=24.7^\circ \) at 295 K to \( \bar{\delta}=24.0^\circ \) at 413 K (averaged for the two inequivalent, quasi-parallel molecules). As a consequence, the linear shift of the pentacene molecules projected along \( a \), \( d_a \), is reduced from 2.05 Å at 295 K to 2.00 Å at 383 K, and the vdW attractive forces acting on the molecules along \( a \) increase. To sum up, pentacene contracts along \( a \) as a result of the increasing librations about the long axis and the smaller herringbone angle (\( \Delta \theta=0.3–0.6^\circ \) per 100 K), supported by the absence of larger librations and translations perpendicular and by the increased attractive vdW forces due to a slightly reduced shift.

Furthermore, the pronounced temperature dependence of the translational motion \( T_1 \) (along the long molecular axis) suggests a tendency to change the relative shift and thus to increase the \( d \)-spacing which is synonymous with a decrease of the tilt angle \( \delta \), giving
Chapter 3. THERMAL EXPANSION IN TC, PC AND RU

Fig. 3.7: Schematic view of the anisotropic expansion in the a,b plane. The libration along the long molecular axis, $L_{11}$, together with a change of the herringbone angle, are responsible for the anisotropic thermal expansion, with $a$ contracting and $b$ expanding.

A consistent explanation for the large value of the (out-of-plane) intermediate expansion eigenvalue.

It can be expected that the effect of increasing vdW forces along the short unit cell axis, and the related change of the tilt angle, as well as the enhanced repulsive interaction from the molecules at the corner to the molecule in the center of the unit cell, are even more pronounced in longer herringbone packed acenes, e.g. hexacene, leading to higher asymmetry and more pronounced uniaxial negative expansion. However, the decreasing stability and the increasing ease of oxidation with increasing $n$, as well as the reported difficulties in growing hexacene crystals with reasonable quality [41] might prevent single crystal studies.

3.3.2 Tetracene vs. Rubrene: The Influence of the Inertial Tensor on the Thermal Expansion

The unit cell parameters for the tetracene and rubrene single crystals at different temperatures are given in table 3.6. Full structure data are available from the CCDC with ref.no. 611392 – 611399.

A comparison of the molecules at 106 K and room temperature for tetracene and rubrene is given in Fig. 3.8a–d, where the size of the C atoms is the 50% thermal motion probability. Hydrogen atoms were not refined, as their scattering power is insufficient for X-rays.

The thermal expansion coefficients along the main axes for tetracene and rubrene are given
Table 3.6: Lattice parameters for tetracene (P\(\bar{1}\)) and rubrene (Cmca) for various temperatures. The unit cell axes are given in \(\text{Å}\), the angles in deg, and the volume in \(\text{Å}^3\).

<table>
<thead>
<tr>
<th></th>
<th>Tetracene</th>
<th>Rubrene</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>106 K</td>
<td>175 K</td>
</tr>
<tr>
<td>(a)</td>
<td>6.0444(6)</td>
<td>6.0493(6)</td>
</tr>
<tr>
<td>(b)</td>
<td>7.7881(8)</td>
<td>7.8253(8)</td>
</tr>
<tr>
<td>(c)</td>
<td>12.4975(13)</td>
<td>12.5283(13)</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>101.029(9)</td>
<td>101.284(9)</td>
</tr>
<tr>
<td>(\beta)</td>
<td>99.496(9)</td>
<td>99.448(9)</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>94.305(9)</td>
<td>94.236(9)</td>
</tr>
<tr>
<td>(V)</td>
<td>566.07(10)</td>
<td>570.25(10)</td>
</tr>
<tr>
<td>(b)</td>
<td>7.1658(3)</td>
<td>7.1737(3)</td>
</tr>
<tr>
<td>(c)</td>
<td>14.2232(5)</td>
<td>14.3189(5)</td>
</tr>
<tr>
<td>(V)</td>
<td>2734.52(16)</td>
<td>2760.18(16)</td>
</tr>
</tbody>
</table>

in Table 3.7, whereas their libration and translation values are listed in Table 3.8. The libration and translation values use the same orthogonal coordinate system as the inertial momentum tensor, that is, the smallest momentum, \(I_1\), corresponds to the long molecular axis \((x_I)\).

Since the tetracene unit cell contains two crystallographically independent molecules, libration and translation values are given for both, and are close in value and relative orientation. Furthermore, the libration and translation directions are relatively closely aligned with the axes of the inertial tensor, with the smallest inertial moment about the long molecular axis. It is clearly seen that the libration about and translation along this axis is the dominant feature.

Due to its non-orthorhombic unit cell, the main axes for the thermal expansion in tetracene are not aligned with \(a\), \(b\) and \(c\), as it is depicted in Fig. 3.9. Axis 1, the direction of the largest expansion, is mostly parallel to \(b\) (26°), perpendicular to \(a\) (87°) and encloses an angle of 127° with \(c\), whereas axis 3 (smallest expansion) encloses angles of approximately 37° with \(a\), 110° with \(b\) and 125° with \(c\). The intermediate axis (2) is perpendicular to the other two. Similar to the other acenes, the largest expansion occurs approximately along the long in-plane crystal axis. In contrast to pentacene (cf. Fig. 3.5), the smallest expansion is strongly turned out of the \(a-b\) plane.

The dense packing in 2-dimensional layers restricts the libration and translation perpendicular to the long molecular axis, allowing large librations about the long molecular axis,
Fig. 3.8: ORTEP-3 drawings [29] of tetracene at 106 K (a) and 295 K (b), and rubrene at 106 K (c) and 298 K (d). The displacement ellipsoids are represented at the 50% level. The directions of the inertial tensor axes system are given in a) and c) by \((x_1, y_1, z_1)\), and, only in tetracene, by \((x'_1, y'_1, z'_1)\) for the second molecule.

And translations along it. Since the herringbone packing of the molecules within a layer produces an asymmetry in the intermolecular interactions, a change in the herringbone angle is expected with temperature, and within the layer the thermal expansion is going to be anisotropic. The herringbone angle in tetracene changes indeed from 51.09(7)° at 106 K to 52.12(6)° at room temperature, which produces the large expansion approximatively along \(b\), i.e. in direction of \(\alpha_1\), and a much smaller expansion perpendicular to it. As a
3.3. RESULTS AND DISCUSSION

Fig. 3.9: Thermal expansion in tetracene: While the main axes of the thermal expansion ellipsoid are parallel to the crystal axes in rubrene, they are tilted with respect to the triclinic unit cell of tetracene. For numerical values of $\alpha'_1$, $\alpha'_2$ and $\alpha'_3$, see table 3.7.

result, the anisotropy in thermal expansion is of order 15–20 in tetracene.

Furthermore, considering equipartition of the translational and rotational energies allows for an estimation of the bonding strengths from the values of $L$ and $T$ in table 3.8 that give the averaged square of the respective excursion (angle): With the translational amplitude $x$ and $E = \frac{1}{2} fx^2$, the relative spring constants $f_i/f_j$ are equal to $T_j/T_i$. From the values of $T$ ($T_i = x^2$) in table 3.8, $f_{2(3)}/f_1 = 1.7(1.9)$, revealing the softer potential for movements along the long molecular axis, i.e. the weaker bonds between the molecular layers, compared to the in-plane forces in tetracene. Similarly, the relative spring constants $D_i^*/D_j^*$ for the librations are equal to $L_j/L_i$ due to equipartition, with $D_{2(3)}^*/D_1^* = 2.5(3.1)$. Since the dominant libration $L_1$ about the long molecular axis is sensitive to the enhanced in-plane forces, the observed anisotropy of the librations is much smaller than expected from the inertial moments ($I_{2(3)}/I_1 = 8.6(9.6)$).

In contrast, rubrene crystallizes in an orthorhombic unit cell, and the main axes of the thermal expansion are therefore aligned with the crystallographic axes. Similar to tetracene, the intermolecular angle (between the tetracene backbones) increases from 61.48° (106 K) to 62.41° (RT), producing an expansion along the long in-plane axis, i.e. $\alpha_1 \parallel c$. Consistently, the smallest expansion is observed along $b$, the shorter in-plane axis. The $a$- and
\(b\)-axes have remarkably close values. The anisotropy is of order 4, indicating a much less anisotropic thermal behavior, consistent with the much smaller anisotropy of the inertial momentum tensor (Tab. 3.1). The values coincide well with recently published results [26].

The differences in thermal expansion are reflected in the overall crystal quality of tetracene and rubrene. Recent double crystal topography studies of rubrene [42] have demonstrated that crystals with narrow mosaic spread of order 0.02 deg or better can be grown reproducibly. Such small mosaic spreads are in general not as easily obtained in tetracene, where rocking curves indicate mosaic spreads of order 0.04°. The more uniform thermal expansion of rubrene does not induce as large a stress/strain in a crystal compared to tetracene, where the anisotropic thermal expansion sometimes even shatters a crystal. Optimizing crystal growth procedures to minimize large thermal gradients and reduce large temperature changes may further reduce the mosaic spread. Since small angle grain boundaries, dislocations, and other structural defects may act as charge traps, a reduction in their respective densities is expected to improve charge mobility and threshold voltages in devices fabricated from single crystals of tetracene and rubrene.

### 3.4 Conclusions

The difference in anisotropy of the inertial tensors is reflected in the thermal expansion of tetracene, pentacene and rubrene. While the expansion is highly anisotropic in the case of tetracene and pentacene with a large anisotropy in the inertial moments, it is more uniform and smaller in the more isotropic rubrene. The large anisotropy of the inertial moments of the molecule, together with the dense packing in 2-dim layers, in effect frustrates the librations and translations perpendicular to the long molecular axis in the acenes. This has a strong impact on crystal quality, since large, anisotropic expansion produces stress/strain fields during the PVT crystal growth procedure and temperature-dependent experiments. Consequently, carefully grown rubrene crystals show — for organic materials — excellent, very narrow rocking curves, whereas in tetracene the rocking width is larger. However,

<table>
<thead>
<tr>
<th></th>
<th>Tetracene</th>
<th>Rubrene</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha'_1)</td>
<td>100.2(8)</td>
<td>76.9(3)</td>
</tr>
<tr>
<td>(\alpha'_2)</td>
<td>32(1)</td>
<td>19.7(3)</td>
</tr>
<tr>
<td>(\alpha'_3)</td>
<td>6.0(8)</td>
<td>13.2(4)</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>138(2)</td>
<td>109.7(5)</td>
</tr>
<tr>
<td>(\rho)</td>
<td>1.305</td>
<td>1.265</td>
</tr>
</tbody>
</table>

Table 3.7: The eigenvalues (main axes \(\alpha'_i\) \([10^{-6}\text{K}^{-1}]\) of the thermal expansion ellipsoid) after transformation to an orthogonal system. The volume expansion coefficient \(\gamma\) is given as \(\sum \alpha_i\). The density \(\rho\) \([\text{g/cm}^3]\) is given for room temperature.
rocking curves around tetracene (00l) reflections tend to give small values, of order 0.02 degrees, but mosaic spreads are expected to be larger in perpendicular directions. In addition, the anisotropic expansion might — besides a sluggish phase transition [43] — be the cause for the shattering upon cooling often observed in tetracene crystals.

A particularity in the series of the acenes is the negative thermal expansion along a, observed in pentacene. Pentacene contracts along a as a result of the smaller herringbone angle (\(\Delta \theta = 0.3 - 0.6^\circ\) per 100 K), supported by the absence of larger librations and translations perpendicular to the long molecule axis due to steric hindrance. Furthermore, a slightly reduced relative shift of the molecules along a with temperature increases the attractive vdW forces along a.
Chapter 4

Metastable High Temperature Phase of Pentacene

Polymorphism is a phenomenon often found in organic materials. In pentacene, several polymorphic structures are observed in thin films. Whereas in powders two polymorphs with a $d$-spacing of 14.1 Å and 14.5 Å are common with different ratios depending on the growth conditions, all recent structure studies on pentacene single crystals have reported only one single phase with $d = 14.1$ Å. We further complete the phase diagram of pentacene by a high-temperature phase transition, which leads to a metastable 14.5 Å phase in single crystals and powder, being identical with the original single crystal structure reported by Campbell et al. [44].

4.1 Introduction

Because the differences in energy between various local energy minima is small [45], polymorphism is quite common for organic molecular materials, e.g. pentacene (see below) or sexithiophene ($\alpha$-6T) which crystallizes in a high- and low-temperature form [46, 47]. Slightly different growth conditions then may determine, in which polymorphic form a material is obtained in the experiment.

For pentacene, two different bulk crystal structures have been reported [22, 23, 24, 44], both triclinic and built from herringbone-packed molecular layers. Except the early work by Campbell et al. [44] (minor revision [41]) who found a structure with a $d$-spacing of 14.5 Å, all recent papers and CCDC entries consistently report on a different triclinic structure with a $d$-spacing of 14.1 Å (overview in ref. [24]), regardless of the growth method (PVT or from solution). This raises the question whether the apparent polymorphism in
pentacene bulk crystals requires the presence of defined impurities during crystallization. On the other hand, both the 14.1 Å and 14.5 Å bulk polymorphs are found in microcrystalline powders [48], and at least four different structures are reported for pentacene thin films, having characteristic \(d\)-spacings of 14.1, 14.4, 15.0, and 15.4 Å (overview in ref. [39])\(^1\), thereof the spacings of 14.4 and 15.4 Å are most frequently observed. Their occurrence is strongly dependent on the deposition conditions, and their different \(d\)-spacings are attributed to varying tilt angles of the molecules with respect to the surface normal (\(c^*\)). In contrast to single crystals, full structures are still unavailable for thin films, despite several groups reporting on in-plane axes (\(a\) and \(b\)) [39, 49, 50], or even on the full unit cell [39, 51]. However, it is expected that the pentacene molecules adopt a layered herringbone-type arrangement. Considering the similar \(d\)-spacing, the 14.4 Å-phase in the thin film is often identified with the (obsolete?) single crystal structure by Campbell [44], and therefore called bulk or single crystal phase. In contrast, the 15.4 Å-phase is known as the thin film phase.

As mentioned above, the two polymorphs (14.1/14.5 Å) are often observed with different volume fractions in powders, as evidenced by Raman spectroscopy and (high-resolution) powder XRD [48]. It was reported that the 14.5 Å polymorph irreversibly transforms into the 14.1 Å polymorph at 0.2 GPa [30]. Recently, it was shown that also single crystals (\(d=14.1\) Å) contain variable amounts of the 14.5 Å phase as impurities, inhomogeneously distributed with an enhanced concentration near the surface [52]. Previously, Monte-Carlo simulations were further employed in order to study the stability of a variety of theoretically possible polymorphs of pentacene, with the two experimentally observed phases (14.1 Å and 14.5 Å) represented by the deepest energy minima [45].

So far, there were no indications for a temperature-induced phase transition in pentacene powder [53] or single crystals. Remarkably, our attempts for high-temperature crystallography on pentacene single crystals (grown by PVT, see section 2.2) always ended in losing the crystals upon heating before enough data for a full structure solution above 110–150 °C could be collected. Either mechanical stress/strain or the existence of a high temperature phase transition were considered as possible explanations for the shattering of the crystals. As a consequence of the mechanical instability of pentacene single crystals upon heating, information on its origin might be found only by powder XRD, since cracking of powder does not affect the measurement. On the other hand, \textit{in-situ} crystallography on freshly grown crystals at high temperature is not practicable.

\(^1\)The exact value of the \(d\)-spacing is dependent on the extraction method, as well as on the calibration. Therefore, phases that differ only by 0.1 Å should considered identical, unless the use of internal standards allows for such absolute precision. Consequently, we do not distinguish between 14.4 Å and 14.5 Å, and either term can be used.
Figure 4.1: Phase transition in pentacene: With increasing temperature, a new phase shows up above 460 K, and dominates at 518 K. The shift towards smaller angles of most of the respective peaks is due to thermal expansion.

4.2 Results

Figure 4.1 shows 2θ-scans at various temperatures. The positions and intensity ratios of the reflections measured at room temperature fit well with the pattern calculated by means of any of the 14.1 Å structures [22, 23, 24]. Due to the change of the lattice constants with temperature, most reflections are shifted to smaller angles, i.e. higher d-spacings, with increasing temperature. Above 460–470 K, we notice the occurrence of additional peaks (indicated by arrows), which belong to a new phase, since they cannot be indexed anymore by means of the low-temperature phase unit cell. With further increased temperature, an increasing fraction of the powder converts into the high-temperature phase, which is, among others, characterized by an increased $d_{00l'}$. Finally, at 518 K, the phase transition is almost complete. By removing the heater, the powder was cooled very rapidly to room temperature again. Thus the high-temperature phase could be partially quenched, giving a mixture of the two polymorphs coexisting at room temperature as shown in Fig. 4.2. Whereas the low-temperature phase could be indexed and refined up to 220°C relatively easily, all attempts to find an unit cell and an indexation for the high-temperature phase
failed due to substantial peak overlap of the two phases.\(^2\)

![Graph showing LT + HT phase and LT phase counts][1]

**Fig. 4.2:** Mixture of the low temperature (14.1 Å) and the high temperature phase (14.5 Å) at room temperature. The pristine powder (lower curve) consists only of the standard low temperature polymorph with a d-spacing of 14.1 Å (within the detection limit of the diffractometer). With increasing temperature, a new phase shows up above 460 K, and dominates at 520 K. By cooling very rapidly to room temperature again, the high temperature phase can be partially quenched, giving a mixture of the two polymorphs as shown in the upper curve.

In order to get higher quality powder data, which would enable the indexing and hopefully even lead to a full structure solution by a Rietveld refinement, measurements with synchrotron radiation were carried out at the ESRF\(^3\). These more sensitive measurements confirmed the sluggishness of the phase transition, and revealed further that the pristine powder (ground crystals) already contained a small amount of the high-temperature phase, in agreement with Refs. [30, 48, 52]. The fractions of the two polymorphs have been estimated as 20:1 at room temperature and 1:20 at 563 K. Despite the higher resolution of the data, no matching indexation for the high-temperature phase was found, again due to substantial overlap of the spectra and due to some parasitic phase contamination.

Since not only the phase transition itself could be the reason for the shattering of single

---

\(^2\)It should be noted that the indexation of a triclinic pattern is non-trivial, requiring immense computational power, especially for brute-force “Monte-Carlo” techniques.

\(^3\)The measurements were done by C. Besnard and P. Pattison, using the Swiss-Norwegian Beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF) Grenoble. The wavelength was 0.71 Å.
4.2. RESULTS

Table 4.1: Lattice parameters for the high (HT) and low temperature (LT) polymorph of pentacene, in comparison with Ref. [44], which has been transformed to the reduced cell (r. c.). The unit cell axes are given in Å, and the angles in deg. The d-spacing [Å] is given for room temperature.

<table>
<thead>
<tr>
<th></th>
<th>LT</th>
<th>HT</th>
<th>HT (r. c.)</th>
<th>Ref.[44] (r. c.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>293 K</td>
<td>478 K</td>
<td>478 K</td>
<td>295 K</td>
</tr>
<tr>
<td>a</td>
<td>6.265(2)</td>
<td>6.119(2)</td>
<td>6.119(2)</td>
<td>6.14</td>
</tr>
<tr>
<td>b</td>
<td>7.777(2)</td>
<td>8.058(2)</td>
<td>8.058(2)</td>
<td>7.93</td>
</tr>
<tr>
<td>c</td>
<td>14.536(3)</td>
<td>15.097(3)</td>
<td>14.926(3)</td>
<td>14.90</td>
</tr>
<tr>
<td>α</td>
<td>76.48(1)</td>
<td>80.88(2)</td>
<td>97.52(2)</td>
<td>96.82</td>
</tr>
<tr>
<td>β</td>
<td>87.67(1)</td>
<td>77.68(2)</td>
<td>100.19(2)</td>
<td>100.53</td>
</tr>
<tr>
<td>γ</td>
<td>84.71(1)</td>
<td>85.89(2)</td>
<td>94.11(2)</td>
<td>94.08</td>
</tr>
<tr>
<td>d_{001}^{RT}</td>
<td>14.1</td>
<td>14.5</td>
<td>14.5</td>
<td>14.5</td>
</tr>
</tbody>
</table>

Crystal samples, but also the inherent stress/strain, a single crystal experiment with a possibly less strained crystal, grown at lower temperature in a closed ampoule in vacuo, was finally successful. Additionally, the much shorter data collection time at the synchrotron was an important factor. The full structure of the high-temperature phase could be solved at 478 K and 513 K. With the unit cell at 478 K, the powder patterns could be indexed subsequently, resulting in lattice constants of the high-temperature phase at room temperature. Interestingly, it turned out by a transformation of the unit cell that it is identical to the one reported by Campbell [44] with a d-spacing of 14.5 Å (cf. table 4.1). Upon closer look, the increased d-spacing is not caused by a further reduction of the tilt angle of the molecules (see section 3.3.1), for the individual herringbone layers remain virtually unchanged. However, the adjacent layers are shifted by (2.88, −1.23, 0.36) Å in an orthogonal coordinate system with x ∥ a and z ∥ c* with respect to the low-temperature phase unit cell (Fig. 4.3). Thus, the vertical component of this shift between the layers accounts for the increased d-spacing. Consequently, the density is slightly reduced in the high-temperature phase, and the 14.5 Å polymorph is metastable at room temperature, as it is supported by the occurrence of an irreversible pressure-induced phase transition into the 14.1 Å polymorph in powder [30].

This rearrangement of the layers in different relative positions, finding another “nesting” configuration, is therefore of so-called martensitic nature⁴. Furthermore, the density of structural defects is expected to strongly influence the kinetics of the phase transition, which indeed proves to be very sluggish. Consistently, the pentacene low- and high-temperature phases coexist even at room temperature in powders, where the number of

⁴Martensite is a (metastable) form of e.g. steel, which is generated by a collective shear motion of atomic layers, i.e. by a diffusionless transition.
defects is expected to be large. This may also be the reason for the difficulty in observing the phase transition in calorimetric experiments, where data from powder showed inconclusive results [54]. In contrast, the phase transition is abrupt for single crystals (albeit not always at the same temperature), often resulting in shattering of the sample.

The thermal expansion tensor of the high-temperature phase pentacene was determined in the range from 373 K to 563 K from powder data (see Fig. 4.4), by the method described in section 3.1. The smallest thermal expansion is approximately along the \(a\)-axis and is slightly negative, with unit strain of \(-3(2) \times 10^{-6} \text{ K}^{-1}\), whereas the intermediate and largest thermal expansion directions lie between the \(b\)- and \(c\)-axes, with values of \(110(10) \times 10^{-6} \text{ K}^{-1}\) and \(133(13) \times 10^{-6} \text{ K}^{-1}\). The small negative thermal expansion is consistent with the negative thermal expansion observed in the low-temperature phase of pentacene, also approximately parallel to the \(a\)-axis (see previous chapter).

The nature of the phase transition is also of interest in thin film growth. Since films often show a \(d\)-spacing of \(14.4/5 \text{ Å}\), they might crystallize in the Campbell/high-temperature phase structure, and are therefore metastable. Thus thin film processing has to take into account that an incomplete phase transition might occur at higher temperature, leading
Fig. 4.4: Lattice constants for the high temperature phase (powder measurements): Whereas $b$ and $c$ expand upon heating, $a$ remains almost constant. With change of the unit cell angles, negative thermal expansion is observed approximately along $a$.

to large stress/strain fields in the films that will induce defect formation.

4.3 Conclusions

We have determined the structure of the high-temperature polymorph of pentacene, which is stable above 478 K. Its structure is consistent with that reported in 1962 [44] and that has not been reproduced since in single crystals. The herringbone-type 2-dimensional layers are identical in both polymorphs, whereas their layer stackings strongly differ. Both polymorphs show uniaxial negative thermal expansion, with direction approximately along their respective $a$-axes. To obtain high-quality thin films or single crystals, it is therefore necessary to minimize the temperature profiles in processing. Surface tension effects may also play a role, since the 15.0 Å and the 15.4 Å thin film polymorphs easily convert to a $d$-spacing of 14.5 Å by dipping films into solvents such as ethanol, where pentacene is not
soluble [55]. Controlling processing parameters during thin film or single crystal growth is therefore crucial as stress/strain fields will influence the polymorphic phase transition(s). The metastability of the high-temperature polymorph will have to be taken into account for device reliability.
Chapter 5

SCLC in Organic Single Crystals: Extracting the Trap DOS and Challenges in Reaching the Trap-Free Limit

In this chapter, we report on densities of trap states (DOS) of pentacene single crystals, experimentally determined by the method of temperature-dependent (TD) SCLC spectroscopy. With the knowledge of the DOS and by comparing the DOS to the corresponding SCLC characteristics, we are able to elucidate challenges associated with (assumingly) reaching the trap-free region. The issue of contact effects is addressed by the extraction of activation energies and their dependence on the applied voltage. Furthermore, influence on the DOS by exposure of samples to either oxygen or X-rays is analyzed.

5.1 Introduction

Space-charge limited current (SCLC) measurements have often been applied as a method to get a measure for the quality of organic crystals in terms of (effective) mobilities and total trap densities [1]. Because the sample preparation and the experimental setup is comparably easy, SCLC methods are more frequently used than time-of-flight (TOF) measurements. Nevertheless, critical issues have to be addressed, such as the quality of the contacts, and geometry considerations. In common to all SCLC based techniques is that ohmic, non limiting contacts are required [10]. Otherwise, contact effects or contact-related defects can significantly influence the measured current, and result in incorrect conclusions.
The interpretation of SCLC data is also very sensitive to the device geometry. Often used is a coplanar sample layout with two (parallel) electrodes on the same sample surface, characterized by the sample thickness $t$ and the electrode–electrode distance $L$ (see Fig. 5.1b). Conveniently, the (main) direction of current flow coincidences in this layout with the direction measured in field-effect transistors (FETs), which is for several materials, such as rubrene and pentacene, the direction of high charge carrier mobility. Because the current density varies strongly over the entire crystal thickness, a valid interpretation of the measured current is highly complex, in particular due to the lack of applicable theoretical results. In contrast, the theory for a sandwich-type device layout (Fig. 5.1a) is well developed (see for example [10]). In this case, the sample consists of a crystal platelet between two electrodes spaced by the crystal thickness $L$. With the cross section area $A$ of the electrodes much larger than $L$, the current is — besides minor edge effects — uniformly confined over $A$. Unfavorably, the direction perpendicular to the crystal platelets is often assigned by a lower mobility. Most straightforward is the analysis of trap-free (tf) SCLC data, where the current $I$ is proportional to the square of the applied voltage $V$, as discussed in the introduction. By applying Child’s law (eq. 1.2), the mobility is then readily calculated. At this point, geometrical considerations play a critical role: While in sandwich-type structures the current relates to voltage and electrode-electrode distance (= sample thickness) as $I \sim V^2L^{-3}$ (Child’s law), coplanar geometry leads to $I \sim V^2L^{-2}$ [57]. Total trap densities have often been estimated using the (more or less) pronounced step in the $I$-$V$ characteristic, which may indicate full trap filling at $V_{TFL}$, prior to reaching finally a $V^2$ behavior [1].

In this work, we go a step further and use temperature-dependent SCLC spectroscopy (see section 1.3 and Refs. [13, 58]) to map the density of (trap) states (DOS) as a function of energy in the gap, without any assumptions on the shape of the DOS. Recently, an amorphous-like density of states with very broad tail states was reported for pentacene single crystals [59]. In contrast, we find a DOS, which is 1–3 orders of magnitude lower in all samples. Furthermore, we can observe narrow band tail states in the best sample, similar to rubrene [58] and a rubrene derivative (chapter 6).
5.2 Experimental

An optimized sample preparation method was found in the “flip-crystal” approach [60], benefitting from the minimized sample handling. Thin crystals (preferred thickness <2 \( \mu \text{m} \)) are placed on glass substrates with 20 nm Au on 5 nm Cr electrode stripes, where they stick by electrostatic adhesion.

A 20 nm gold top electrode is then evaporated onto the crystal, which is slightly cooled during the evaporation (\( T_{\text{Mask}} = -5 \) to \(-10^{\circ}\text{C} \)) to minimize thermal damage. The overlap of the electrodes results in a typical cross section of \( A \sim 1.5 \cdot 10^{-5}\text{cm}^2 \). Finally, electrical connections were made with silver epoxy (EPOTEK EE 129-4, hardening over night at room temperature in a flow of argon) and 25 \( \mu \text{m} \) gold wires from the contacts on the glass substrate to the sample connector print. A small drop of silver epoxy was used to connect the top electrode on the crystal with its continuation on the glass substrate. Thanks to the transparent glass substrates, a few of the samples could be inspected with crossed polarizers under the stereo microscope with transmitted light to control the domain structure. The thickness of the crystals was measured by atomic force microscopy (AFM) as optical inspection by a line-plate in the high magnification (40x) ocular of a stereo microscope turned out to be unreliable for crystals below env. 10 \( \mu \text{m} \).

The electrical measurements were performed in a LEYBOLD closed-cycle cryostat in inert helium atmosphere and in darkness, covering a maximal temperature range of 30–350 K. By the use of helium exchange gas, a constant sample temperature, measured at the back side of the sample holder, could be reliably adjusted with a resistive heater coil (driven by a LAKESHORE 331/340 controller). Since SCLC measurements required an instrument that is capable to resolve currents in the range of a few femtoamps, a KEITHLEY 6517A electrometer was used. It also features a built-in voltage source of up to \( \pm 1000\text{V} \). For the ultrathin crystals, the range of \( \pm 100\text{V} \) with higher resolution was used, as 10–20 V were sufficient to force a current of 1 \( \mu \text{A} \) (even at lowest temperature), which was chosen as a current limit not to damage the sample. With the usage of an internal scanner card for the electrometer, several samples and/or several cross sections on the same crystal could be measured consecutively without changing the plugs. The sample holder with five triaxial plugs and wires allowed for four channels to be used for the bottom contacts (on \text{LOW/GND})\), with the top contact connected to \text{HIGH}. By a proper shielding, leakage

\footnote{An exact value for the sample thickness \( L \) is essential for the absolute DOS.}
currents well below 1 pA at 100 V were achieved. To inject holes from the bottom contacts, negative voltage was applied at the top contact; $V > 0$ results in hole injection from the top contact.

The typical measurement procedure for TD-SCLC was as follows: After initial tests at room temperature, the samples were ramped down with a rate of 0.5–2 K/min to the lowest temperature, typically 100 K. Prior to the measurement of the current-voltage characteristic (at each chosen temperature), an initial delay of 20 min ensured thermal equilibrium. The $I$-$V$ curves were measured by a stepwise increase of the applied voltage and measuring the quasi-equilibrium current. A current measurement delay of 10 s turned out to be sufficiently long compared to the settling time of the system. Typically 30-50 points were measured per voltage decade. Since it turned out to be relevant to obtain reproducible results in rubrene [58], initially all of the samples were warmed up to room temperature intermediately in order to empty filled traps and to reach the same starting conditions for the measurement at the next higher temperature. However, in pentacene the detrapping was found to happen within few minutes at most even at lowest temperature. Therefore, in most pentacene samples TD-SCLC could be measured considerably faster, omitting the intermediate ramping back to room temperature. Usually, the temperature was changed in the range from 100–220 K with an interval of 10 K (see Fig. 5.3). At higher temperatures, the broadening of the Fermi statistics has a negative influence on the spectroscopic character of TD-SCLC. Especially shallow states can only be reliably measured at low temperature. Sometimes, the temperature range had to be reduced even further in the analysis in order to obtain thermally activated (Arrhenius) behavior.

The extraction of the density of trap states, $h(E)$, and the reconstruction of the energy axis, according to eq. 1.4–1.9, was performed by running MATLAB code [61]. For the calculation of higher order derivatives of the experimental $I(V)$ curves according to eq. 1.6, a smoothing spline fit was applied to the measured data (keeping the fit within 1% of the raw data) in order to prevent the deconvolution from diverging due to discontinuities. Also $E_A(V)$ was smoothed ($<1–10\%$ deviation from raw activation energies). Additionally to the DOS, the effective mobility $\mu_{\text{eff}}(E)$ was calculated, which allows for an estimation of the intrinsic microscopic band mobility $\mu_0$ by extrapolation of $\mu_{\text{eff}}(E)$ to the band edge ($E=0$).

---

2Original thermo-modulated (TM) SCLC by Schauer, Nespurek et al. varies the temperature in a range of a few Kelvin only.
5.3 Results and Discussion

To determine the quality of the sandwich structures, $I$-$V$ characteristics have been recorded at room temperature for several cross sections on a device. By interchanging the electrical connectors or by switching the sign of the applied voltage (if using the scanner card), both the laminated (bottom) and the evaporated (top) electrode could be chosen as the injecting contact. While several cross sections on the same sample lead to almost identical current values, the magnitude of the measured current is strongly dependent on the nature of the injecting electrode, i.e. the direction of current flow.

Typical examples are given in Fig. 5.4 and 5.5 (inset): With the laminated contact as injecting contact ("lam"), the current is several orders of magnitude higher than in the case where the charge is injected from the evaporated top electrode ("evap"). Nevertheless, also in the latter case an “ohmic” contact behavior in the sense of slope 1 in the log($I$)-log($V$) plot is observed. Going to higher voltages, the current injected through the top electrode is approaching the higher values for the case of laminated injection electrode.
Fig. 5.4: Room temperature current-voltage characteristic for a typical pentacene device. By interchanging the electrical connectors, the injecting electrode can be chosen. With the laminated contact as injecting contact ("lam"), the measured current is several orders of magnitude higher than in the case where charge is injected from the thermally evaporated top electrode ("evap").

only in very few samples. This first simple test clearly shows a contact limitation when using the evaporated electrode as the injecting contact. This asymmetry of the contacts have been observed in all our samples (pentacene, rubrene [58], and a rubrene derivative (chapter 6)) except one pentacene sample which has been stored in a glove box for 1 month prior to the measurement, possibly showing a long term annealing effect for the top electrode or degradation of the laminated bottom contacts. On the superiority of laminated contacts has also been reported by others [62, 63].

Although the laminated contacts are superior to the evaporated electrode, this difference is not sufficient to assure the absence of contact limitations. Unlike text book behavior, constant slopes of 1 in the log(I)-log(V) plot are required, but not sufficient to indicate ohmic behavior of the contact. A much stronger criterion is the dependence of the activation energy (\(E_A\)) on the applied voltage. For a hole conductor, the position of the quasi Fermi level (\(E_F\)) is shifted from a position within the energy gap to the valence bandedge by applying a voltage (compare Fig. 1.3). Thus, \(E_A\) has to (monotonically) decrease with increasing voltage. Deviations from this monotonic behavior therefore indicate injection problems. Another, even harder criterion for current limited only by the space-charge and
not by the injecting contact is the thickness dependence of the current ($I \sim L^3$). However, such measurements are not applicable to our samples, since they show a too large crystal-to-crystal variation in terms of DOS and effective mobility, even within one batch [61]. As an example, Fig. 5.5 depicts the voltage dependence of $E_A$ for sample Pc03.2 (thickness: 250 nm), showing strong contact effects up to 0.2 V in this sample, even for the “better” (laminated) contact. For further evaluation of the data, leading to the DOS finally, only the “clean” parts of the $I-V$ characteristics with $V$ above the contact limiting range were used. A comparison with the room temperature $I-V$ curve (inset) shows that an apparently “ohmic” current is not enough to proof the absence of contact effects.

![Fig. 5.5: Activation energies $E_A$ extracted from temperature-dependent $I-V$ characteristics for the sample Pc03.2 (laminated injecting contact). The inset shows room temperature measurements of the same sample.](image)

In the following, we concentrate on sample Pc03.1 (thickness: 165 nm). Figure 5.3 shows the $I-V$ characteristics for sample Pc03.1 measured for temperatures between 100–210 K ($\Delta T=10$ K). We observe a very steep increase of the current ($\propto V^{27}$ max!), indicating a low (deep) trap density. Further, at the lowest temperatures, the kink observed in the $I-V$ characteristics could be caused by a steeply increasing trap density. This is further supported by the pinning of $E_A$ above 0.8 V (inset).

As described, we derive the density of trap states (localized states) from the $I-V$ characteristics, and establish an energy scale using the extracted activation energies and ap-
plying a correction for the statistical shift (Eq. 1.9).\(^3\) The DOS for Pc03.1 is depicted in Fig. 5.6. The overall density is low (\(\sim 10^{16} \text{ cm}^{-3}\text{eV}^{-1}\)) enough to reveal band tail-like states, approaching \(10^{20-21} \text{ cm}^{-3}\text{eV}^{-1}\) at the band edge (extrapolation of the data to \(E_D=0\), assumption of exponential tails). The estimated DOS of \(10^{20-21} \text{ cm}^{-3}\text{eV}^{-1}\) at the band edge is in reasonable agreement with the calculated band structure for pentacene [4] (0 K, polymorph “5A-M”).

![Fig. 5.6: DOS for sample Pc03.1. From the deep states (\(\sim 10^{16} \text{ cm}^{-3}\text{eV}^{-1}\)), band tail-like states emerge, approaching the band edge (\(E=0\)) at \(10^{20-21} \text{ cm}^{-3}\text{eV}^{-1}\). For comparison, the amorphous-like density of states reported by Lang et al. [59] is plotted, including fits for bulk and surface (FET) band tails.](image)

The characteristic energy of these band tails is \(kT_e \sim 20\text{ meV}\), which is slightly higher than that reported for rubrene (11 meV) [58], and very similar to a rubrene derivative sample (see section 6.3.3).

Since the observed band tail states are narrow in comparison with amorphous inorganic materials [64], we do not only ascribe their origin to static, amorphous-like disorder, but also to dynamic fluctuation of the structure, i.e. thermal motion of the molecules. A comparison of the molecular thermal motion of pentacene and rubrene (see chapter 3) suggests that the width of the band tail states might be influenced by the respective

\(^3\)It has been shown that this correction is small for low densities of traps resulting in a steep current increase [61].
amplitudes of the thermal motions. However, this explanation is rather speculative as it is not clear yet if the measured tail states are representative for highest quality pentacene and rubrene single crystals, and no clear temperature-dependence of the tails was observed. On the other hand, the effect of thermal motion on charge transport by fluctuations of the intermolecular coupling has been theoretically studied and calculated recently [65, 66]. It is shown that dynamic (thermal) disorder is able to localize charge carriers efficiently. Troisi et al. conclude that the effect of thermal disorder on the intermolecular transfer integrals can be the missing ingredient in the description of transport in organic semiconductors [66].

Knowing the DOS of a sample, we can further discuss the \(I-V\) characteristics, for example at room temperature, more precisely. For instance, we note for Pc03.1 that the band edge is still far away at room temperature, since the Fermi level is shifted into the rising band tail states at lowest temperature\(^4\) only (see Fig. 5.3). Owing to the existence of band tails in the DOS, much more charge would have to be injected to fill all states in the tails in order to shift \(E_F\) right into the valence band. From the extrapolation of the band tail states to \(E_D=0\) eV, we can estimate the number of charge carriers to fill all traps as \(N_t \sim 10^{20-21}\) cm\(^{-3}\) eV\(^{-1}\) \(\times kT_e =2\times10^{18}-10^{19}\) cm\(^{-3}\). From this number, we estimate a \(U_{TFL}\) of \(N_teL^2/\varepsilon_r\varepsilon_0 = 2.8 - 28\) V. For comparison, a current of 1 \(\mu\)A is reached in Pc03.1 below 0.4 V at room temperature (see inset of Fig. 5.7), and also at lowest temperature (100 K) we do not exceed 1.3 V. For the rubrene derivative sample 2 (see section 6.3.3) a \(U_{TFL}\) of \(>300\) V is calculated from an extrapolation of the band tails, resulting in a (trap-free) current density of \(>5000\) A/cm\(^2\) for a mobility of (only) \(10^{-3}\) cm\(^2\)/Vs. Obviously, such high voltages will lead to field strengths and current densities which — by far — exceed the limits any of our samples could hold out.

\section*{5.3.1 Influence of X-rays on the DOS}

The creation of deep traps by exposure to X-rays has been reported for rubrene FETs [67]. To resolve these states quantitatively and in energy, we carried out TD-SCLC measurements on several organic materials. Based on some indefinite results in rubrene bulk [61], several pentacene and rubrene derivative samples were exposed to X-rays (CuK\(_\alpha\), 40 kV/30 mA) in order to elucidate the influence of high energetic, ionizing X-ray radiation on the density of trap states. During the exposure, the samples were held in inert argon atmosphere to exclude degradation by oxygen or water. Correct positioning of the sample in the frontally striking beam was ensured by fluorescent marks above and below

\(^4\)At higher temperatures, the current limit of 1 \(\mu\)A is reached at lower voltage, i.e. smaller shift of \(E_F\), due to increased thermal activation of the charge carriers.
In general, both room temperature \( I-V \) curves and the DOS were distinctly altered by exposure to X-rays during 1–4 hours. The inset of figure 5.7 shows room temperature \( I-V \) measurements before and after 2 hours of exposure. While in the “ohmic” part of the characteristic the current is reduced by one order of magnitude, the trap filling region is shifted to higher voltages, pointing to an increased trap density. Consequently, the trap density is increased by more than one order of magnitude after the exposure to X-rays (Fig. 5.7). Also the effective mobility is clearly affected by the increased trap density, as depicted in Fig. 5.8. After the X-ray exposure, the mobility extrapolated to \( E_D=0 \) is \( \sim 10^{-3} \text{cm}^2/\text{Vs} \), compared to at least \( \sim 10^{-1} - 1 \text{cm}^2/\text{Vs} \) in the initial sample. This effect was most pronounced in highest quality samples showing band tail states, whereas only minor changes could be observed in samples with higher initial trap concentrations. Similarly, prolongation of the X-ray exposure did not notably change the DOS further.

Since the DOS is changed in a broad energy range, we can exclude purly chemically active defects as the origin of the increased DOS. More likely, structural defects are introduced, either by an increased disorder or by chemically inactive impurities, created by radiation induced reactions. However, the presence of reactive oxygen or water at the ppm-level
cannot be excluded, although the samples were mounted for the experiment in a glovebox and held under Ar during the exposure to X-rays. As a result of crack formation due to thermal stress at the crystal/glass interface, several attempts failed to simultaneously measure the DOS in a second sample on the sample holder as a reference, which was never directly exposed to the beam.

### 5.3.2 Influence of oxygen to the DOS

By controlled exposure to oxygen, a stable and energetically sharp hole trap state at 0.27 eV above the valence band could be created in rubrene single crystals [58], consistent with a reaction of $^{1}$O$_2$ and rubrene to the corresponding endoperoxide [68]. In order to investigate the influence of oxygen on the DOS in pentacene, similar experiments were carried out: After extracting the DOS of the pristine sample (Pc02.4) as a reference, the sample was directly exposed for several hours (at room temperature and in darkness) to $^{1}$O$_2$ and O$_3$ by exciting molecular oxygen with UV light in the vicinity of the sample. Subsequent $I$-$V$ measurements at room temperature (in He again) show indeed a strong influence of oxygen exposure on the characteristic (Fig. 5.9): The current *increases* on
continued exposure time. Since the increase in current is observed in both contact configurations, we can exclude surface or contact effects as its origin. Obviously, oxygen acts as an acceptor (hole dopant), creating additional holes and shifting $E_F$ closer to the band. Doping by oxygen was also observed by Jurchescu et al. [69].

![Figure 5.9: Current-voltage measurements at room temperature on increasing exposure time to $^1\text{O}_2/\text{O}_3$ (measured in He atmosphere). Oxygen acts as an acceptor, increasing the current in the “ohmic” region by 3 orders of magnitude.](image)

Surprisingly, the DOS does not drastically change upon exposure to oxygen and ozone (Fig. 5.10), and also the effective mobility remains unchanged. This suggests that no hole traps are created by $^1\text{O}_2$ or $\text{O}_3$ within the lower part of the band gap, or that the defects are metastable, disappearing within a few hours, i.e. during the TD-SCLC measurement. Due to the long measurement timescale, TD-SCLC is apparently not suited for detecting metastable defects. For the same reason, efforts in visualizing hydrogen-related defects [70, 71] in the DOS of pentacene by TD-SCLC were unsuccessful. The absence of damage to the sample on exposure to reactive oxygen species stays in contrast to newest findings for pentacene thin films [72] (in press). Possibly, there would be a distinct effect on the DOS, when starting with an even lower DOS, as observed in Pc03.1 upon exposure to X-rays (see Fig. 5.7).
5.4 Conclusions

The density of bulk trap states in highest quality pentacene single crystals is as low as \( \sim 10^{16} \text{ cm}^{-3} \text{eV}^{-1} \) at 0.2–0.5 eV from the band edge. Further, we observe the onset of an exponential band tail with \( E_c \sim 20 \text{ meV} \) in the best sample. Overall, the trap density in pentacene crystals is about 1 order of magnitude higher than in rubrene and in a rubrene derivative (see Fig. 8.1).

Extended exposure to ionizing X-rays influences the DOS of very clean samples significantly. As there is no formation of discrete trap levels as a sign for chemical defects, but an over-all increase of the DOS by one order of magnitude below 0.3 eV, we suppose structural defects as the origin of the increased broad in-gap DOS. These defects could origin from impurities (created by radiation-induced reactions) which do not act as hole traps.

By taking into account the large number of states in the narrow band tails, we showed that it is very difficult to shift \( E_F \) into the valence band and thus to actually reach the trap-free limit in a SCLC experiment.

---

Fig. 5.10: DOS before and after exposure to \(^{1}\text{O}_2\)/\( \text{O}_3 \) (measured in He atmosphere). There are only small changes in the density of trap states.
Chapter 6

Electrical Properties of a New Rubrene Derivative

The relation between molecular packing and mobility is highlighted in this chapter by a comparison of rubrene to one of its derivatives in terms of crystal structures and field-effect mobilities. Furthermore, the rubrene derivative crystals have been characterized by temperature-dependent SCLC in order to obtain the density of trap states, as a measure for the electrical quality.

6.1 Introduction

Unsubstituted, linear acenes have been at the center of organic molecular crystal research for the past decades due to their model character for the study of electrical and optical properties [5], and due to the promise of pentacene thin films as a thin film transistor material [73]. Recently, rubrene has joined this selection as several groups have reported a charge mobility in field-effect devices near or above 10 cm$^2$/Vs [27, 28, 67, 74, 75]. Unlike pentacene, which is one of the small molecules of choice for thin film applications, rubrene does not readily form crystalline ordered films, neither by evaporation nor by solution-based deposition. Recently, however, ordered rubrene films were produced using alternative methods: evaporation onto a pentacene film as substrate [76], and by incorporation of rubrene into a polymer matrix [77]. From a technological standpoint, it is desirable to synthesize derivatives of rubrene that would easily form high-quality thin films, with the promising electrical properties of unmodified rubrene.

It is commonly assumed, and supported by calculations, that an increased intermolecular $\pi$-orbital overlap increases the bandwidth, and thus the mobility [1]. Therefore
structures with π-stacking rather than the prevalent herringbone packing are expected to show higher mobilities [78]. Accordingly, several new materials have been chosen or designed. Successful examples are the functionalized pentacene derivatives [79] (which show as solution-deposited films field-effect mobilities as high as 1 cm²/Vs [80]) and rubrene, as already mentioned above. Recently, a direct correlation between structure and mobility has been reported for various tetrathiafulvalene derivatives, crystallizing in three types of structures [81]. In contrast, almost no effect of (small) changes in the packing on the mobility has been observed for various tetracene derivatives [82].

In this study, we have synthesized a new modification of rubrene, grown single crystals, determined the crystal structure, and measured the electric properties. Of the two polymorphs growing, one (1) has a structure drastically different from the packing of unsubstituted rubrene, with a strongly twisted tetracene backbone and enhanced spacing between them. No field-effect is observed with crystals of polymorph 1. On the other hand, polymorph 2 shows a field-effect mobility as high as in rubrene, indicating a similar in-plane packing. As crystals of polymorph 2 have always grown as very thin platelets, the full structure is not known. Nevertheless, as it exhibits a very similar d-spacing compared with an other high-mobility rubrene derivative, we presume the structure to be closely related. The density of electronic states (DOS) in the band gap has been measured using the method of temperature-dependent space-charge limited current (TD-SCLC) spectroscopy. The crystals of polymorph 2 are of very high electric quality with trap densities as low as \( \sim 2 \times 10^{15} \) cm\(^{-3}\)eV\(^{-1}\) at \( \sim 0.2 \) eV from the mobility edge, and a steep exponential rise associated with band tail states on approaching the band edge.

6.2 Experimental Section

Single crystals of 5,11-bis-(4-tert-butyl-phenyl)-6,12-diphenyl-naphthacene [bis-(5,11-parat-butyl)rubrene, 5,11-BTBR, C\(_{50}\)H\(_{44}\), see figure 6.1] have been grown by physical vapor
transport [17] at 260°C, using high purity argon as the transport gas. The crystals are transparent orange colored platelets, typically 0.1–2 µm thick. Only at slightly higher temperature (and with longer growth time), a few bulky crystals could be grown for full structural characterization with XRD.

Field-effect transistor (FET) measurements and TD-SCLC spectroscopy were used to gain insight to the electronic properties of this material. SCLC was measured perpendicular to the surface of the 5,11-BTBR platelets in a sandwich-type sample layout (typical cross section ∼ 1.5 · 10⁻⁵ cm²) with bottom electrodes (Au/Cr) evaporated on a glass substrate, and a Au top electrode evaporated directly onto the crystal. FETs were fabricated in a flip crystal technique, where source and drain electrodes (Au) were deposited on the surface of an oxidized Si wafer, and the crystal is carefully placed on these contacts. A monolayer of OTS was applied to improve the device performance [83]. Typical device dimensions were L=100 µm and W=200–800 µm. More details about the FET measurement technique is described elsewhere [28], whereas experimental details for TD-SCLC can be found in section 5.2. To exclude environmental influence, all electrical measurements were performed in a helium atmosphere.

6.3 Results and Discussion

6.3.1 Structure

Two polymorphs, 1 and 2, have been identified. The lattice constants are listed in table 6.1 for polymorph 1, while for polymorph 2 only the d₀₀₁ spacing (= 35.1 Å) is known. Remarkably, the tetracene backbone of the 5,11-BTBR molecules is significantly twisted in polymorph 1, with a twist angle of 43 degrees between the two opposite C-C bonds at both ends of the backbone (c.f. fig. 6.1). Figure 6.2 shows the molecular packing of 5,11-BTBR (1). The molecules form a layered structure, similar to linear acenes such as tetracene (cf. Fig. 3.1) with the tetracene backbone standing upright. The symmetry (P₂₁/a) is higher compared to e.g. tetracene and pentacene (P₁), and four molecules are in the unit cell (Z=4) in two layers along the c-direction (c=23.53 Å). The tetracene backbones are further apart with in-plane lattice constants of a=17.76 Å and b=9.02 Å, compared with the in-plane axes of roughly 8 Å×6 Å for the unsubstituted acenes. With these large in-plane spacings, the in-plane arrangement differs from the classical herringbone structure, resembling more to a π-stacking structure type, albeit without short-distance interactions.

| a   | 17.764(2) |
| b   | 9.028(1)  |
| c   | 23.527(3) |
| β   | 95.928(4) |
| V   | 3752.8    |

Table 6.1: Lattice constants of polymorph 1.
In contrast, the (unmodified) rubrene molecules have a nearly perfectly planar tetracene backbone, and the arrangement of the molecules differs from the classical herringbone structure: The long axis of the tetracene backbone lies in the molecular planes, enabling π-stacking in direction of the b-axis\(^1\), as depicted in Fig. 6.2. (Crystallographic data for rubrene: see chapter 3.)

The structure of polymorph 2 could not be solved so far, as the material seems to exclusively grow as ultra-thin platelets. From measurements of the d-spacing perpendicular to the extended crystal surface, we can assume a structure closely related to the one found for

\[^1\text{We use a different space group setting (Cmca) than e.g. Sundar et al. [27] or Goldmann et al. [28] (Acam), resulting in the interchange of the axes.}\]
6.3. RESULTS AND DISCUSSION

a constitutional isomer, 5,12-BTBR [84, 85]. (5,11-BTBR and 5,12-BTBR can be clearly distinguished by the respective $^{13}$C-NMR signals.) In this case, the in-plane arrangement of the molecules is very similar to that of rubrene, with even shorter distances between the tetracene backbones (3.55 Å compared to 3.74 Å). However, the addition of the $t$-butyl groups increases the interlayer spacing by 31%. Similar to rubrene, it leaves the backbone almost perfectly planar (see fig. 6.2).

In FET measurements the current flows within the $a$, $b$-plane of 5,11-BTBR, while in SCLC it flows perpendicular to the molecular layers.

6.3.2 Field-effect transistor measurements

A typical output characteristic for a 5,11-BTBR (2) FET is shown in Fig. 6.3 (upper panel.) The observed hysteresis is very small, indicating that trapping/releasing effects between two successive measurement sweeps over 20–30 seconds are negligible. The turn-on voltage $V_{on}$ and threshold $V_t$ are below 8 V and 5 V, respectively, in typical samples. The mobilities were calculated using the standard MOSFET equation for the drain current in the saturation regime at an effective gate voltage of -10 V. In all devices with OTS-treated oxide, the mobility exceeds 1 cm$^2$/Vs, and a maximum mobility of 12 cm$^2$/Vs was observed in the best sample. Temperature-dependent measurements have been performed on a representative device. The resulting values for the mobility are shown in Fig. 6.3 (lower panel). We note a small decrease of $\mu$ (from 5.7 cm$^2$/Vs to $\sim$1.8 cm$^2$/Vs) when cooling from room temperature to 160 K. $V_{on}$ and $V_t$ also decrease from 8 V to 5 V and 4 V to 1.2 V, respectively. After warming-up to room temperature, the measured characteristics as well as the mobility are within 10% of the original measurements. No change of the performance is observed after storing the device in inert atmosphere for one month.

In rubrene the distance between the positions of the C-atoms of two backbones is as short as 3.75 Å (edge molecule to middle one), and 3.85 Å (edge to edge molecule, zigzag along $a$). Taking the known structure of 5,12-BTBR as a model for the structure of 5,11-BTBR (2), we can expect in-plane backbone-backbone distances comparable to rubrene, i.e. 3.5 Å to 3.9 Å. As the relevant bandwidth in a crystal is determined by the details of the HOMO and LUMO wave functions, a careful electronic structure calculation is needed to quantify small differences in band structure associated with variations in packing geometry (e.g. pentacene [4, 86]).

The measured mobility in the 5,11-BTBR (2) single-crystal devices might be reduced compared to the intrinsic bulk values by surface or interface effects. We find, however, a distinct direction-dependence of the mobility on the crystal surface [85], and thus we
conclude that the FET measurements reflect to a significant degree the bulk properties.

The shortest backbone-backbone distance in 5,11-BTBR (1) is not shorter than 6.5 Å, which is commonly expected to drastically reduce the π-overlap and thus the bandwidth. Norton and Houk [87] have calculated that the twist of acenes (Anthracene–Heptacene) basically does not change the HOMO-LUMO energies, i.e. the energy gap is not affected. On the other hand, a too large twist will affect the aromaticity of the molecules, increasing the localization of charge on the molecule. Experimentally, a twist of 144° has been observed in a pentacene derivative [88]. Consequently, we are not able to measure any field-effect mobility in 5,11-BTBR (1).
6.3. RESULTS AND DISCUSSION

6.3.3 TD-SCLC measurements

In the previous section, the performance of 5,11-BTBR devices in terms of high field-effect mobilities has been presented. Another important measure for the intrinsic electronic quality is the density of (trap) states, since electrical transport is known to be severely affected by charge carrier trapping even in the best organic crystals. To quantify the DOS, we applied the method of temperature-dependent space-charge limited current (TD-SCLC) spectroscopy \[13, 58\], described in section 5.2, to crystals of 5,11-BTBR (2).

The DOS is reflected in the shape of the measured \(I-V\) curves. Temperature-dependent measurements are needed: 1) as an appropriate method to assess the possible influence of contacts at low voltages, and 2) in order to associate a given applied voltage with the corresponding distance of the quasi-Fermi level from the band mobility edge. This is done by measuring the activation energy \(E_A(V)\). As the Fermi level is moved toward the band edge with increasing voltage, \(E_A\) has to be decreasing monotonically with increasing voltage. Contact-limited current is thus recognized as a deviation from this monotonic dependence of \(E_A\) upon \(V\). Additionally, abrupt changes in the density of states are recognized, since e.g. discrete trap levels lead to a pinning of \(E_A\). Because of the asymmetry of DOS(\(E\)) around \(E_F\), \(E_A\) is corrected to \(E_D\) (dominant energy) by the statistical shift. The current-voltage characteristics measured at room temperature for several samples of 5,11-BTBR (2) have in common, that a pronounced, steep increase of the current occurs at relatively low voltage, indicating the trap-filling SCLC region. Additionally, a gradual transition to \(I \propto V^2\) is observed for most samples. This is a first evidence for a low over-all trap density. The observation of \(I \propto V^2\) dependence, however, does not, by itself, indicate that the trap free range has been reached. The quantitative analysis of the DOS with energy resolution \(\sim kT\) by the means of TD-SCLC is therefore still needed. Due to thermo-mechanical stress during temperature cycles in the course of the TD-SCLC measurements, several crystals suffered from cracks, interrupting the top electrode or directly affecting the measurement cross-sections. Two complete sets of data are discussed here (sample 1: \(d=1.25\ \mu m\), sample 2: \(d=0.4\ \mu m\), \(A=1.5 \cdot 10^{-5}\ cm^2\) for both samples.)

The current-voltage characteristics for sample 1 and sample 2 for selected temperatures are plotted in figure 6.4. For sample 1, the curve measured at 300K shows three distinct regions: (sub)ohmic current at low voltage, trap filling SCLC, and apparently “trap-free” SCLC at highest voltage. For low temperatures, only the trap filling and the “trap-free” region are observed, because the ohmic current is too small to be measured with our measurement setup. At low temperatures, the increase in current during trap filling is very steep with slopes of up to 18 in the \(\log(I)\)-\(\log(V)\)-plot. Arrhenius-plots of the temperature dependent data reveal thermally activated behavior for \(\sim 0.2 V \leq U \leq 5\ V\) (sample 1), and
Chapter 6. PROPERTIES OF A RUBRENE DERIVATIVE

At room temperature, three regions can be discerned in sample 1: A (sub-)ohmic behavior, dominated by contact effects (for $V \leq 0.3$ V), then a steep increase, and finally a turn-over to a constant slope of 2 in the log-log plot. For lower temperatures, $V^2$ behavior is still reached, after a very steep increase proportional max. $V^{18}$. The $V^2$ behavior is due to the quasi-Fermi level moving in the exponential part of the density of states ("band tail states"), but the trap-free limit is not yet reached. For the extraction of the DOS($E$), $I$-$V$ curves measured between 130 K and 180 K have been used ($\Delta T = 10$ K.) Inset: $I$-$V$ curves for sample 2. Below 0.34 V, where the current is contact-limited, as well as above 3.3 V, close to the rollover to a $I \propto V^2$ behavior, the current is not thermally activated. Thus meaningful activation energies can be extracted only in this intermediate range. Consequently, only data represented by straight lines was used for the extraction of the DOS($E$).

For 0.34 V $\leq U \leq 3.3$ V (sample 2). At lower voltage, both Arrhenius plots and subohmic $I$-$V$ characteristics indicate a current limitation by the injecting contact. At highest voltage, log($I$) does not depend linearly on $1/T$, as the quasi Fermi level moves within $\sim kT$ to the mobility edge. Thus extraction of $E_A$ is limited to this intermediate voltage range.

The extracted DOS for both samples is shown in figure 6.5. In the range from 0.15 to 0.3 eV, the over-all density of trap states is low, in the range of $\sim 10^{15}$ cm$^{-3}$eV$^{-1}$. On approaching the mobility edge ($E=0$), tail-like states with a characteristic energy of 22 meV (sample 2), and possibly the onset of a band tail for sample 1 emerge. Too close to

![Graph showing current-voltage characteristics for different temperatures and samples.](image-url)
Fig. 6.5: The density of states toward midgap is in the range of $10^{15}$. Close to the band edge, the DOS increases in a way reminiscent of band tail states (sample 2). Within 2–3$kT$ to the mobility edge, the analysis starts to fail, causing an unphysical roll-over of the DOS (open symbols).

the band, where $E_D$ becomes close to $kT$ (i.e. 25 meV at room temperature), the analysis fails, leading to an unphysical roll-over of the DOS. In comparison with rubrene [58], the DOS is as low as in the best rubrene samples, as well as the widths of the band tails are very similar. Worth mentioning is the fact that the DOS reported here is several orders of magnitude lower than the one for pentacene [59], which was measured in a coplanar contact geometry which may emphasize the higher trap densities near/at the surface of the crystal. TD-SCLC spectroscopy on high-quality pentacene crystals indeed exhibits comparably low densities of states as in rubrene and 5,11-BTBR (2), albeit one order of magnitude larger (cf. chapter 5).

A raw measure for the band mobility $\mu$ in 5,11-BTBR (2) along the $c$-axis is taken from extracted effective mobilities $\mu_{\text{eff}}$, a purely numerical construct defined as the mobility at the band edge multiplied by the ratio of mobile to total injected charge (eq. 1.10). Extrapolated to the band edge ($E_D=0$), $\mu_{\text{eff}} \approx 10^{-3}–10^{-1} \text{ cm}^2/\text{Vs}$ in 5,11-BTBR (2). A comparison with rubrene shows values in the same range for $\mu_{\text{eff}}(E_D=0)$ perpendicular to the molecular layers [61], despite the enhanced inter-layer spacing in the derivative.
6.4 Conclusions

Single crystals of a new rubrene derivative have been grown and the semiconducting polymorph 2 has been electrically characterized. The trap density in the energy gap is of the order of $10^{15} \text{cm}^{-3}\text{eV}^{-1}$; low enough to reveal band-tail like states with a characteristic energy of 22 meV. This low DOS and the occurrence of narrow band tails are characteristic for high-quality organic crystals. Presumably having a similar crystal structure and in-plane arrangement of the molecules compared with rubrene, 5,11-BTBR (2) has shown a comparably high in-plane field-effect mobility of up to $12 \text{cm}^2/\text{Vs}$. It fits into the present understanding of the relation between structure and mobility that the in-plane mobility is too low to be measured in 5,11-BTBR (1) because the tetracene backbones are twice as wide apart from each other compared with rubrene, and π-stacking of the backbones is absent.

In order to get a better understanding of the relationship between crystal structure and charge transport, the full structure of 5,11-BTBR (2) and, based thereon, band structure calculations are needed. Additionally, several other new modifications of rubrene are subjects of the ongoing research.
Chapter 7

Iodine Intercalation in Pentacene
Thin Films and Single Crystals

7.1 Introduction

The control of band filling in organic narrow-band materials offers access to a rich phase diagram that straddles the boundaries between metals, insulators, and, eventually, superconductors. In their native, undoped state, most molecular organic crystals are band insulators or semiconductors, with a gap $\Delta$ of order $\sim 1$ eV opening between the HOMO and LUMO bands. Their bandwidth $W$ is typically of order at most a few $100 \text{meV}$ at low temperature, but reduced to $1\text{–}10 \text{meV}$ at room temperature [7]. $W$ is thus much smaller than $\Delta$. This behavior is fundamentally different from wide band semiconductors like silicon, and potentially opens up a host of new correlation phenomena. However, in order to see unusual electronic behaviour, we have to depart from the band insulator at integer filling.

Bulk chemical doping of insulating (or semimetallic) host compounds is one route to introduce charge into the bands of organic semiconductors. This approach has been particularly successful for doped polyacetylene [89], intercalated graphite [90], and doped $C_{60}$ [91, 92]. Graphite intercalation has been intensely studied for several decades, and controlled doping with (earth) alkaline atoms, and other intercalants can induce both metallic and superconducting behavior. Similarly, alkaline doping of $C_{60}$ leads to a number of fullerene compounds, notably those of the $A_3C_{60}$ variety, that show metallic behaviour [91], or superconductivity [93] up to $T_c = 40 \text{K}$ in $C_3\text{C}_{60}$ [92].

There has been considerable interest to extend these studies to the oligoacenes, in particular pentacene. These materials have over the past few years emerged as prototype
small molecule organic semiconductors. The HOMO and LUMO orbitals are formed by the delocalized $\pi$-electrons on the linear benzene ring backbone, which provide perhaps the conceptually simplest example of delocalized molecular orbits. Pentacene takes on a special role since it possesses the smallest bandgap, and is most easily handled, amongst the oligoacenes that are commercially available. Its comparatively high room-temperature mobility of $1.5–5 \text{cm}^2/\text{Vs}$ (Refs. [28, 73, 94, 95]) also makes it an important candidate and reference material for plastic electronics. Finally, interest in the oligoacenes is also driven by the predicted metallic [96] or superconducting [97] behavior of polyacene, i.e. the “infinite linear oligoacene”, a hypothetical compound.

Bulk charge doping of pentacene and a few other oligoacenes by alkaline and halogen intercalation has been studied in some depth by Minakata et al. [98, 99, 100, 101, 102, 103] and others [104] in the 90’s. They discovered that pentacene thin films are readily intercalated by iodine, forming a stage-1 structure\(^1\), with some inconclusive evidence for the existence of a stage-2 compound [104]. Intercalation yields in-plane room temperature conductivities of up to $150 \Omega^{-1}\text{cm}^{-1}$, corresponding to an (estimated) charge mobility of $0.47 \text{cm}^2/\text{Vs}$ [99]. The conductivity is extremely anisotropic, and usually decreases at low temperatures in a fashion reminiscent of disorder-driven variable range hopping. Quasi-metallic behavior of the conductivity in the temperature range from 240 K to 4 K has been reported for few samples only [99]. Pentacene is also intercalated by certain alkaline metals [102], leading to metallic conduction below room temperature, as reported recently [105]. In contrast, tetracene does not seem to intercalate, unless in the state of a tetracene/pentacene composite [106].

That work, however, concentrated exclusively on thin films, rather than bulk single crystals. More recently, the topic was resumed by Ito et al. [107] who reported on the structure of iodine-intercalated pentacene (based on the comparison of measured and simulated powder diffraction pattern), and, most notably, by Brinkmann et al. [108]. Their extensive study contains results for thin film and powder samples, and – for the first time – also for single crystals. In addition to electrical resistivity and XRD measurements, they applied combined studies such as UV/VIS, IR and Raman spectroscopy, as well as ESR spin susceptibility measurements. In contrast to the prior work, they observed the stoichiometry not to be fixed at all, and only a small fraction of the induced holes to be delocalized (in the HOMO band).

However, part of these conductivity studies and all of the X-ray diffraction (XRD) measurements were carried out after intercalation, with the sample out of partial pressure equilibrium with its environment. This is quite problematic given that the temperature

\(^1\)Stage-$i$ means that the intercalants occupy every $i$. interlayer spacing.
scales for pentacene intercalation are vastly different – much closer to room temperature – than for, say, C_{60} or graphite, so that under ambient conditions the intercalant in pentacene is quite volatile and far from frozen in.

In this chapter, we report on in situ structural and conductivity studies of pentacene intercalation, in both thin films and single crystals. This enables us to address the intercalation dynamics, staging issues, and the structural intercalation phase diagram. For iodine-doped pentacene, we find that both thin films and single crystals intercalate easily, but are only found in an effectively metallic stage-1 structure across the whole temperature–partial pressure phase diagram. In alkali doped metal-phthalocyanines, for comparison, an insulator-metal-insulator transition was recently found on progressive intercalation [109], a behaviour that can be assigned to band filling – this effect is entirely absent in pentacene.

For pentacene thin films, we find that successive intercalation and desorption induces an irreversible and controlled change in the polymorph of the crystalline structure. Finally, we also observe quasi-metallic conductivity, in line with the Mott-Ioffe-Regel limit [110, 111]. Intercalated single crystals show a quasi-metallic behavior of the conductivity as well, although their structural degradation due to the iodine intercalation, as monitored by the width of the respective rocking curve, is much more pronounced compared to thin films. From preliminary Hall measurements, we derive a hole mobility of 0.4 cm^2/Vs and a concentration of free carriers of 1 \times 10^{21} \text{ cm}^{-3} for an intercalated thin film with an estimated stoichiometry of (PEN)I_{22,0.5}. These numbers point out that i) the transferred charge is only partially mobile in the HOMO band, and ii) the band mobility is reduced compared to the pristine film on which a field-effect mobility of 1 cm^2/Vs has been measured prior to the iodine intercalation.

7.2 Experiment

As iodine-intercalated pentacene is most stable when it is kept in its partial pressure equilibrium in an iodine vapor environment, in-situ studies are preferable. The samples were kept in a closed glass container with electrical feedthroughs and a X-ray transparent window made of kapton foil. The chamber was evacuated to a pressure of 10^{-2}–10^{-4} mbar prior to the exposure to iodine in order to degas the pentacene crystal or thin film. Separated by a teflon valve, iodine crystals served as an iodine reservoir. The vapor pressure of iodine could be adjusted in a range of 1 \times 10^{-2} to 1 mbar by controlling the temperature of the iodine source material by a thermo-electric element, or, alternatively, by resistive heating (for temperatures above room temperature.)

The experimental setup was mounted on top of the omega table of a STOE STADI P powder
diffraction planes parallel to the sample surface could be measured \((00l)\) reflections). The PSD allowed for short \(\theta-2\theta\) scan times, with a typical duration of 4-5 minutes for a range of \(20^\circ\) in \(2\theta\). For very small crystals \((50 \times 200 \times 3 \, \mu m^3)\), the scan time had to be increased up to 10 minutes.

Electrical measurements were carried out mostly in a four-probe arrangement using two Keithley 236 SMUs, which provide a high input impedance of \(10^{14} \Omega\) in order to cover the high resistive initial state as well. Additionally, a thin film in Hall-bar geometry was measured with a Hewlett-Packard 4155 parameter analyzer up to fields of 1.5 T. Details about the room temperature Hall measurements will be published elsewhere [112].

Both, electrical and XRD measurements, were made \textit{in-situ}, and, for single crystalline samples, simultaneously. The temperature dependence of the resistance was measured separately, after remounting the sample to a home-made dip-stick cryostat.

Pentacene thin films with a thickness of 40–60 nm were grown by thermal evaporation at a rate of \(0.3 \, \text{Ås}^{-1}\). During the evaporation the pressure was in the range of \(10^{-6}\) mbar, and the glass (or oxidized Si wafer) substrates were held at 70°C. Pentacene single crystals were grown by horizontal physical vapor transport [17], with Argon of 6.0 purity as transport gas (see section 2.2).

Gold electrodes for two- and four-probe measurements were defined by thermal evaporation through a shadow mask. For thin films, we exclusively used a top contact layout, while for single crystals both top and bottom contacts (the latter in a “flip crystal” approach as described in the previous chapters) were utilized. Since iodine reacts with conductive silver epoxy by formation of (non-conductive) AgI salt, gold paste (Ted Paella Inc.) and colloidal graphite (“Aquadac”) was used for the bonding with 10–50 \(\mu m\) gold wire.

7.3 Results

7.3.1 Structure

The \(d\)-spacing for pentacene thin films before intercalation matches the published values of 14.5 Å of the “bulk” phase and – more rarely – 15.4 Å (“thin film” phase). In single crystals, the observed \(d\)-spacing is 14.1 Å [24]. The iodine intercalation process sets in shortly after exposure to iodine vapor, as it is monitored by XRD. Figure 7.1 shows the time evolution of the diffracted intensities in a thin film experiment, performed at room temperature. In addition to the original \((00l)\) peaks of the pure pentacene, new peaks
7.3. RESULTS

Fig. 7.1: Intercalation dynamics, measured by in-situ XRD θ-2θ scans. The diffracted intensity is color-coded, the diffraction angle 2θ (and the d-spacing, respectively) is drawn on the vertical axis, and the time is shown on the horizontal axis.

(00l′′) originating from the intercalated part of the sample appear at equally well defined, smaller values of 2θ. The d-spacing of the intercalated phase is thus drastically enhanced to 19.4±2 Å for thin films (in good agreement with the previous studies), and 19.2±2 Å for single crystals, which is consistent with ref. [107], but considerably larger than the value of 18.2±4 Å reported in ref. [108] for single crystals. The diffraction peaks originating from the intercalated phase remain intense up to large values of l′′, corresponding to a slowly decaying form factor, which reflects the dominant electron density in the thin iodine layers between the pentacene molecules. Whereas the whole film thickness contributes to the measured intensities for both the pristine and the intercalated phase, the strong absorption of X-rays by iodine (Z=53) limits the absorption depth to 1–4 µm (4° ≤ 2θ ≤ 20°), and thus the scattering volume, in intercalated pentacene, assuming (PEN)I₂ as the nominal composition.

We find intercalation times for thin film samples that are reproducible and comparable to the previous studies in the literature. In contrast, the variation for single crystal samples, and the timescale itself, is larger. There is a strong dependence of the intercalation dynamics on the degasing period prior to the exposure to iodine, as well as on the crystal quality. The former observation points to the fact that gas molecules other than iodine might already be present in the pristine crystals, e.g. argon as a left-over of the crystal growth or oxygen, as reported in the literature [69]². The latter can give us indications on

²Oxygen, also if intercalated during the sample preparation into the first few layers only, would hinder iodine from entering.
the intercalation mechanism (see section 7.4).

In both thin film and single crystal samples, a slow decrease of the diffracted intensity from the intercalated phase is observed after a maximum has been reached. It should be noted that the conductivity is still increasing during this slow decay of the X-ray signals (cf. section 7.3.2). While single crystalline samples completely lose their crystallinity upon long-time exposure to iodine vapor, the XRD signal at least of some of the thin films hardly changed even after five weeks in iodine saturated atmosphere\(^3\). On the other hand, exposure to air reduces the diffraction intensities due to the desorption of iodine.

Evaluating the rocking curves was considered a valid method to assess the sample quality from a structural point of view, since their widths reflect the mosaic spread of the crystal domains. While both the pristine and the intercalated phase give rise to sharp peaks in \(2\theta\) (0.1–0.2\(^\circ\) FWHM in films, 0.04–0.06\(^\circ\) FWHM in high-quality crystals), they strongly differ with respect to their widths in \(\omega\): The best values measured for the 001 and the 002 reflection of the original pentacene crystal are <0.05\(^\circ\) FWHM in \(\omega\) (see Fig. 7.2). This excellent value for the original phase is retained during the intercalation process (until

\[^3\]Electrical measurements could not be carried out after a few days because the solder joints had been corroded by the aggressive iodine vapor.

Fig. 7.2: Rocking curves for the pristine phase (001, 002) and the intercalated phase (001–004) of a pentacene single crystal. FWHM is 0.05\(^\circ\) for the pristine pentacene and is retained during intercalation for the non-intercalated part, while the iodine intercalated phase shows FWHMs of >1\(^\circ\), remaining nearly constant as well.
the signal from the pristine phase disappears). In contrast, the intercalated phase shows rocking widths (FWHM) of $\approx 1^\circ$ for the same crystal from the beginning, indicating a drastic loss of crystal quality due to the intercalation of iodine. The broadening is much less distinct in thin film samples with FWHMs of 0.15–0.2$^\circ$ (pristine) and 0.5–0.6$^\circ$ (intercalated phase) for a high-quality film. This distortion of the sample by the intercalation process is in contrast to the observation by Minakata et al. [98] for thin films, where the crystallinity was enhanced by the iodine intercalation. One can speculate that Minakata et al. may have started with a worse film quality, which enabled a realignment of the grains during the intercalation. On the other hand, decreased widths in $2\theta$ do not necessarily point to small widths in $\omega$.

The very narrow rocking widths for some of the pristine crystals have another consequence, as already depicted in figure 2.5 of the experimental section: Due to the scanning mode with a non-continuous movement of the $\omega$ position, the measured intensities and their ratios are highly dependent on the adjustment of $\omega_0$, as it determines at which (single) point of the rocking curve the intensity is integrated during the $\theta/2\theta$ scan. Therefore, ratios between the intensities of $001/002/003/\ldots$ can change notably. Intensities originating from the intercalated phase, $00l''$, are much less affected because the rocking curves are broader than the step in $\omega$.

Whereas intercalated graphite shows a variety of staging, there is no experimental evidence in our data for staging other than stage-1, neither in pentacene thin film nor in single crystalline samples. In the thin film experiments, a rough intercalation phase diagram (map of the equilibrium film structure) as function of the sample temperature $T_{\text{PEN}}$ and the iodine source temperature $T_{\text{IOD}}$ (i.e. the iodine vapor pressure $p_{\text{IOD}}$) has been obtained (Fig. 7.3). In the same way, the stage-dependent stability regions of a number of alkaline and halogen intercalates of graphites have been established previously, although the relevant temperature scales for graphite intercalates are much higher [113]. Our effort is hampered to some extent by minor irreversible effects, as discussed below. Nevertheless, Fig. 7.3 shows the rough location of the phase boundary between the pristine and the “fully” intercalated

---

Footnotes:

4 These values should not be taken as absolute values (see footnote in section 2.3).

5 The width in $\omega$ for a perfect powder sample is $360^\circ$ (sic!).
phases. We never observed higher stage compounds for any of the \((T_{\text{PEN}}, T_{\text{IOD}})\) values that we analyzed.

Upon closer look on our data on a logarithmic intensity scale, traces of a second intercalated phase with a \(d\)-spacing of 18.0±2 Å were observed in about 50\% of the studied single crystal samples. The weak 00\(l''''\) reflections start to show up after the main intercalated phase (00\(l''\)) with \(d=19.2\) Å has already been substantially established, and disappear gradually again.

For thin films, the intercalation is, within limits, a reversible process. One of these limits is the sample degradation on continued iodine exposure, which is irreversible. Full desorption to within the detection limits of our XRD setup is only achieved at temperatures above about 80°C. In the case of single crystals, full desorption of the iodine could be achieved by simultaneous heating and vacuum pumping as well, but not without the complete loss of crystallinity, i.e. the pristine pentacene is not recovered.

Surprisingly, another phenomenon was observed for pentacene thin films during the intercalation/desorption experiments described above: When the initial film consisted mainly of the “bulk” phase \((d_{001}=14.5\) Å), it was transformed almost entirely into the “thin film” phase \((d_{001}'=15.4\) Å). This surprising result means that the reversible intercalation process can be used to control the polymorphism of pentacene.

### 7.3.2 Conductivity

During the iodine intercalation the in-plane resistance of the sample undergoes a massive over-all drop of 7–9 orders of magnitude, as depicted in Fig. 7.4 for a thin film sample and in Fig. 7.5 and 7.6 for single crystals. The decrease of the resistance is most pronounced at the early stage of the process, and flatens out at an intermediate stage, with a minimum resistance of 0.01–1 \(\Omega\)cm in thin films. The degradation of the sample due to extended exposure to iodine is displayed by the slowly increasing resistance after having reached the “optimum” concentration of iodine. When single crystals are exposed to iodine vapor with a vapor pressure of 0.07 torr (corresponding to a temperature of the iodine reservoir of 8°C), the in-plane resistance saturates at an intermediate level. Further increasing of \(p_{\text{iod}}\) leads to a decrease in resistance (Fig. 7.5). We do not ascribe this to staging or band filling effects, rather to percolation of highly conducting (i.e. richly intercalated) parts of the sample, since evidence for staging is completely absent in the simultaneous XRD measurements. As X-rays probe the bulk, the diffraction intensities do not follow the stepwise increase of the iodine vapor pressure. It is notable that the in-plane resistivity in single crystal samples still continues to decrease for hours after the diffraction peaks have
Fig. 7.4: Typical time-dependence of the in-plane resistance during the intercalation process (thin film sample). Intercalation causes the resistivity to drop over seven orders of magnitude. After reaching a resistivity of typically 10–100 mΩ·cm, the conductivity is not further improved by continued exposure to iodine; instead a gradual worsening of the conductive behavior is observed, probably related to the structural degradation observed in XRD.

reached their maximum values. Overall, we do not observe a cascade of staging compounds, or a sequence of different electronic states like in the alkali doped metal-phthalocyanines [109].

A simultaneous measurement of the resistance perpendicular and parallel to the surface of a pentacene crystal reveals an electrical anisotropy of more than 7 orders of magnitude (see Fig. 7.6), in agreement with the values reported for thin films in ref. [101]. This huge anisotropy is expected since the iodine ions (I$_3^-$) intercalate between the molecular layers, interrupting the (small) π-overlap in pentacene perpendicular to the molecular layers. For the same reason, it is difficult to extract exact resistivity (conductivity) data from measurements of crystals (and thick films): With a bottom contact ("flip-crystal") geometry, virtually only the first layer of the crystal is directly in touch with the contacts$^6$, whereas several layers of pentacene have direct contact to the thermally evaporated top-contacts due to Au intrusion and diffusion. Only if the current contacts cover the side faces of the crystal, the whole crystal cross-section will equally contribute to the current — but only in the case of homogenous doping. Therefore, the effective resistivities (conductivities) of iodine-intercalated pentacene crystals are estimated from a comparison with thin-film samples, and according to their temperature-dependence (see below). As a side-remark, the contact resistance is decreased by the iodine intercalation as well.

$^6$There may be some diffusion of Au into pentacene from the bottom contacts as well, albeit — at room temperature — of negligible extent.
The variation of the in-plane bulk resistivity $\rho$ with temperature is quite small for most samples, as shown in Fig. 7.7. For comparison, thin-film data from Ref. [101] are plotted as well. The Arrhenius plot of $\log \rho$ vs. $1/T$ reveals not a straight line as expected for a gapped insulator, but a behavior more reminiscent of variable range hopping, as suggested previously in the literature [101]. The values of $\rho$ at room temperature for the thin-film samples in this study are very similar with those reported in Ref. [101]. The lower the
7.3. RESULTS

Fig. 7.6: Resistance and diffraction intensities vs time (crystal). The in-plane resistance, the resistance perpendicular to the molecular layers, and the θ/2θ-scans have been measured simultaneously. The side faces of this crystal were covered with epoxy, leaving only the top face directly accessible for the iodine vapor. The in-plane resistance follows the stepwise increase of the iodine vapor pressure, while the resistance perpendicular remains high.

At room temperature the more “metallic” appears its temperature dependence, i.e. the smaller its increase with decreasing temperature. The uncorrected resistivity values even of thin crystals are much higher than for average thin films if we simply take the entire cross section of the crystal to calculate ρ from the resistance R. Nevertheless, the intercalated crystals show metallic behavior in the sense of dρ/dT ≥ 0 below 150 K. For some samples, the resistivity at low temperature is smaller than at room temperature. Consistent with our considerations about the huge directional anisotropy of the resistivity (see above) and its effect on the effective current flow, we recalculated the resistivity for the single crystal samples by adjusting an effective cross-section such that the resistivity at room temperature fits into the qualitative temperature dependence in Fig. 7.7.

Furthermore, we observe a hysteresis in the resistivity due to some spontaneous desorption of iodine, particularly at temperatures above 200 K. If a partially desorped sample is measured again, not only its resistivity at room temperature is higher than before, but the temperature dependence of the resistivity turns to more insulator-like behavior. This experiment again points to the importance of a sufficiently high initial conductivity of the samples in order to observe a quasi-metallic state. Recently, the same observation was
made in alkaline-doped pentacene [105]: The metallic state could only be observed after annealing the sample, which increased the conductivity by 3–6 orders of magnitude to a value of 10–20 mΩ·cm, remarkably similar to the values reported here.

Although some of our heavily doped crystals can be considered as metals in the sense of \( dρ/dT \geq 0 \), the sheer amount of intercalated iodine needed for metallic behavior is unexpected. Thus the number of induced mobile holes must actually be much lower than expected from an iodine content exceeding that of the host material. As electron spin resonance (ESR) measurements have indeed shown [108], a large fraction of the induced charge seems to be localized on the individual pentacene molecules — especially at high doping, being stabilized by the strong polarization of the pentacene molecules by the negatively charged \( I^-_3 \) counterions. In order to obtain an estimation for the actual amount of free charge, we performed Hall measurements on a fully intercalated thin film sample, with an initial field-effect mobility of 1 cm²/Vs in the non-intercalated state. Since its resistivity was as low as 0.02 Ω·cm, the measured Hall voltage, \( V_H \), was expected to be small and close to the resolution limit of the measurement setup (10 µV). Therefore, the applied current was increased to 100 µA to allow for sufficient resolution of the measurement [112].

![Graph showing temperature-dependent resistivity](chart.png)

Fig. 7.7: Temperature-dependent (4-probe) resistivity of iodine-intercalated pentacene thin films and single crystalline samples. A cross-over from insulating to quasi-metallic behavior occurs around 10 mΩ·cm room temperature resistivity. For thin films, the cross-section is the whole film thickness, for single crystals the cross-section has been estimated as described in the text.
Averaged for $\pm I$ and $\pm B$, $n_h \approx 1 \times 10^{21}$ cm$^{-3}$ and $\mu \approx 0.4$ cm$^2$/Vs. Consequently, only 50% of the charge induced by $I_3^-$ (at an estimated, nominal composition of (PEN)I$_2$) is mobile, resulting in an effective doping of $\sim 1/3$ hole per pentacene molecule, but the (band) mobility has decreased$^7$, most probably due to unfavorable structural changes – also in-plane – in the company of the intercalation. It is known for pentacene thin films that the mobility is inversely correlated to the rocking curve width [5], further supporting our findings.

7.4 Discussion

There is agreement in the literature that the intercalated iodine is present as $I_3^-$ ions in the highly conductive, “intermediate” doping compound (and as $I_5^-$ in an even higher doping stage, not observed here.) Little evidence exists for the presence of “unreacted” I$_2$, apart from Ref. [107], where also the existence of $\Gamma^-$ ions in intercalated pentacene is postulated. For all these different iodine species, a very similar ionic radius of about 4 Å is expected, leading to a corresponding increase of the $d$-spacing [114]. Even so, in our studies we always find similar values of 19.2–19.4 Å, irrespective of the initial $d$-spacing. The increase by 4.9 Å for “bulk phase” thin films and by 5.1 Å for single crystals, respectively, can only be explained by a simultaneous phase transition within the pentacene layers: The tilt angle between the pentacene molecules and $c^*$ is thereby decreased, approaching the “thin film” structure, in which the molecules stand nearly perpendicular on the $a$-$b$ plane.

As a consequence of this simultaneous phase transition probably leading to additional stress/strain (chapters 3 and 4), the structural quality of thin films and single crystals with pristine $d$-spacings of 14.5 Å and 14.1 Å, respectively, is more likely to be seriously affected by the iodine intercalation than in the case of “thin-film phase” samples with $d=15.4$ Å. Experimentally, this structural degradation is most obvious in the distinct broadening of the rocking curve of high-quality single crystalline and “bulk phase” thin film samples. To what extent a subsequent thermal annealing can recover the original sample quality should be subject of further studies. We note in this context that an additional annealing step has been found to be crucial for high conductivity values in alkaline doped pentacene, enabling metallic behavior of the conductivity [105].

As the high anisotropy in conductivity perpendicular and parallel to the molecular layers indicates, the electrical conductance of iodine-doped pentacene is strongly two-dimensional. Intuitively comprehensive from the anisotropic structural change, ab-initio calculations of $^7$The intrinsic band mobility of pure pentacene films may be higher than the reported field-effect effective mobilities, since a substantial amount of the induced charge might be trapped in a FET device.
the band structure and the charge transfer in doped pentacene further reinforce the experimental observations of two-dimensionality theoretically [115]. Whereas $I^-\text{ leaves the pentacene band dispersion within the plane almost unchanged, just shifting the Fermi energy } E_F \text{ slightly below the valence band edge, } I_3^- \text{ introduces bands with large dispersions, which are attributed to the hybridization of the } I_3 \text{ wave functions. Common to both dopant cases is that the bands are flat along } Z-\Gamma (\parallel c^*).$

The mechanism of iodine intercalation in pentacene is still an open question, even though there cannot be any doubt about the diffusive type. From our measurements, we can give a few qualitative, at most semi-quantitative answers. Firstly, when we compare experiments on crystals to those on thin films, the overall timescale to reach a saturation of the XRD intensities, as well as later on a minimum in the resistivity, is always longer in crystals. Particularly perfect crystals — with respect to their optical appearance and the line/rocking widths in XRD — often require particularly long exposure times to reach the minimum resistivity. This points to a diffusion mechanism which implies grain boundaries, since their number is highest in thin films and lowest in high-quality crystals (that still may consist of several perfectly homogeneous crystalline domains.) It is known that diffusion along grain boundaries is faster than pure bulk diffusion. Since the iodine is incorporated in between the pentacene layers, lateral diffusion (parallel to the pentacene layers) might be dominant at the first glance. Rather to the contrary, the diffusion through the larger crystal faces, perpendicular across the molecular layers and along grain boundaries, is dominating, as it comes out from a simple calculation of the evolution of the relative XRD intensities for both phases as a function of the doping profile, and consequently of the time. The time evolution of the XRD intensities for the intercalated structure thereby strongly resembles the time evolution of the oxygen content in pentacene crystals exposed to dry air, monitored by weight uptake [69]. Jurchescu et al. found the typical diffusion length to be of the order of the crystal thickness. However, some details in our XRD measurements, e.g. a sneaky onset of the diffraction intensity and the transition to saturation and subsequent or simultaneous degradation, strongly depend on the individual sample and could not be fitted by a simple diffusion model. However, the absolute iodine content has not been determined in this study (e.g. by the weight uptake). Therefore, it is not possible to extract a precise value for the diffusion constant; nevertheless, by comparing our structural and electrical results to those in the literature, we can reasonably estimate the iodine content in intercalated thin films and crystals as $(PEN)_2I_{2-2.5}$ in the minimal resistance state.

Another possible mechanism important in the very early stage of the iodine intercalation is suggested by the time evolution of the in-plane resistance. The initial drastic decrease in resistance in most samples may originate from a charge transfer to iodine before it
finally intercalates the pentacene. Since such a surface adsorption/charge transfer process should then be expected for all our samples, irrespective of the previous outgassing, we instead propose the following explanation: The formation of $I_3^-$ from $I_2$ already occurs during the diffusion of iodine through the surface and along the grain boundaries, before it is intercalated between the molecular layers at a fixed position.

While we do observe, on progressive intercalation, first a rapid decrease in resistivity and then again a gradual increase, we ascribe the latter increase to sample degradation and disorder, as supported by XRD evidence, and not to the formation of a Mott insulating state.

### 7.5 Conclusions

In this chapter, we reported on *in situ* structural and conductivity studies of pentacene intercalation by iodine, in both thin films and single crystals. This enabled us to address the intercalation dynamics, staging issues, and the structural intercalation phase diagram.

For iodine-doped pentacene, we find that both thin films and single crystals intercalate easily, but are only found in an effectively metallic stage-1 structure across the whole temperature-partial pressure phase diagram. Due to the insertion of the $I_3^-$ ions between the molecular layers, the system becomes strongly 2-dimensional, as reflected in the huge anisotropy in the resistivity within and perpendicular to the layers of $>10^7$. For pentacene thin films, we find that successive intercalation and desorption induces an irreversible and controlled change in the polymorph of the crystal structure. Intercalated single crystals show a quasi-metallic behavior of the conductivity as well, although their structural degradation due to the iodine intercalation, as monitored by the width of the rocking curve, is much more pronounced compared to thin films. From Hall measurements, we derive a hole mobility of $0.4 \text{cm}^2/\text{Vs}$ and a concentration of free carriers of $1 \times 10^{21} \text{cm}^{-3}$ for an intercalated thin film with an estimated stoichiometry of (PEN)I$_2$. These numbers point out that *i*) the transferred charge (2/3 charge per pentacene, i.e. $2 \times 10^{21} \text{cm}^{-3}$) is only to 50% mobile in the HOMO band, and *ii*) the band mobility is reduced compared to the pristine film on which a field-effect mobility of $1 \text{cm}^2/\text{Vs}$ has been measured prior to the iodine intercalation.
Chapter 8

Conclusions and Outlook

Several aspects of charge transport in organic molecular crystals have been addressed in this thesis, including the density of trap states, chemical doping and the relation between molecular packing and mobility. Trap states are due to chemical impurities or structural defects. Whereas chemical impurities can be reduced by suitable purification of the source material, structural defects may be inherent to the crystal growth process. Thereby large, anisotropic thermal expansion in the weakly bonded crystals is crucial. Similarly, the pronounced thermal motion of the molecules implies a dynamic disorder, resulting in fluctuations of the intermolecular transfer integral and increased charge carrier localization. Increased static disorder is often observed in organic materials as an undesirable consequence of chemical “doping”, which is entirely different from conventional doping in inorganic materials, resulting in the formation of a new dopant/host compound. Nevertheless, a large amount of charge can be induced. Since the bandwidth is dependent on the overlap of the molecular orbitals in the crystal, the details of the crystal packing are essential for observing high intrinsic charge carrier mobilities.

The large, anisotropic expansion of order $100 \times 10^{-6} \text{K}^{-1}$ (linear) has a strong impact on the crystal quality, since stress/strain fields are produced during the crystal growth by physical vapor transport and temperature-dependent experiments. The large anisotropy of the inertial moments of the molecule, together with the dense packing in 2-dim layers, in effect frustrates the librations and translations perpendicular to the long molecular axis in the acenes. The difference in anisotropy of the inertial tensors is reflected in the thermal expansion of tetracene, pentacene and rubrene. While the expansion is highly anisotropic in the case of tetracene and pentacene with a large anisotropy in the inertial moments, it is more uniform and smaller in the more isotropic rubrene. Consequently, carefully grown rubrene crystals show — for organic materials — excellent, very narrow rocking curves, whereas in tetracene (and pentacene) the rocking width is larger. In addition, the
anisotropic expansion might — besides a sluggish phase transition — be the cause for the
shattering upon cooling often observed in tetracene crystals.

A particularity in the series of the acenes is the negative thermal expansion along \(a\), observed in pentacene. Pentacene contracts along \(a\) as a result of the smaller herringbone angle (\(\Delta \theta = 0.3 \sim 0.6^\circ\) per 100 K), supported by the absence of larger librations and translations perpendicular to the long molecule axis. Furthermore, a slightly reduced relative shift of the molecules along \(a\) with temperature increases the attractive vdW forces along \(a\).

Furthermore, we have determined the structure of the high temperature polymorph of pentacene, which is stable above 478 K. Its structure is consistent with that reported in 1962 [44] and that has not been reproduced since in single crystals. The herringbone-type 2-dimensional layers are identical in both polymorphs, whereas their layer stacking strongly differs. The high-temperature polymorph shows uniaxial negative thermal expansion as well, with direction approximately along the \(a\)-axis. To obtain high-quality thin films or single crystals, it is therefore necessary to minimize the temperature profiles in processing. Controlling processing parameters during thin film or single crystal growth is therefore crucial as stress/strain fields will influence the polymorphic phase transitions. The metastability of the high-temperature polymorph will have to be taken into account for device reliability.

The density of bulk trap states (DOS) was derived by temperature-dependent SCLC spectroscopy. In highest quality pentacene and rubrene derivative single crystals the DOS is as low as \(\sim 10^{16} \text{cm}^{-3}\text{eV}^{-1}\) and \(\sim 10^{15} \text{cm}^{-3}\text{eV}^{-1}\), respectively, at 0.2–0.5 eV from the band edge. Furthermore, we observe the onset of an exponential band tail with \(E_c \sim 20\) meV in the best sample. Overall, the bulk trap density in pentacene crystals is higher than in rubrene [58]. On the other hand, it is several orders of magnitude smaller than the values reported for the surface of pentacene and rubrene crystals (cf. Fig. 8.1). In the case of pentacene, the existence of the 14.5 Å phase as an impurity in the crystals with \(d=14.1\) Å [52] might be an important factor for the increased bulk trap density compared to rubrene, besides the more anisotropic thermal expansion and larger thermal motion. Since the impurity phase is observed near the surface in higher concentrations [52], it might partly be responsible for the high trap density at the surface of pentacene crystals.

Extended exposure to ionizing X-rays influences the DOS of very clean samples significantly. As there is no formation of energetically discrete trap levels as a sign for chemical defects, but an over-all increase of the DOS by one order of magnitude below 0.3 eV, we suppose structural defects as the origin of the increased in-gap DOS. These defects could origin from impurities (created by radiation-induced reactions) which do not act as hole
Fig. 8.1: Tail states in the DOS has been observed for samples of pentacene, rubrene and a rubrene derivative. Required for the experimental observation of tail states is a low deep states density. In our best samples, we find at 0.4 eV a density of $10^{16} \text{ cm}^{-3} \text{ eV}^{-1}$ in pentacene, and $10^{15} \text{ cm}^{-3} \text{ eV}^{-1}$ in rubrene [58] and the derivative. Compared to these bulk trap densities, the density of traps near/at the surface of organic crystals is enhanced: Lang et al. [59] used a coplanar photoconductivity measurement setup, and Goldmann et al. [116] derived the interface trap density from bias stress measurements on rubrene FETs.

traps. By taking into account the large number of states in the narrow band tails, we showed that it is unlikely to shift $E_F$ into the valence band and thus to actually reach the trap-free limit in a SCLC experiment.

Since the observed band tail states are narrow, we do not only ascribe their origin to static, amorphous-like disorder, but also to dynamic fluctuations of the structure, i.e. thermal motion of the molecules. A comparison of the molecular thermal motion of pentacene and rubrene suggests that the width of the band tail states could be influenced by the respective amplitudes of the thermal motions. However, this explanation is rather speculative as it is not clear yet if the measured tail states are representative for highest-quality pentacene and rubrene single crystals. On the other hand, the effect of thermal motion on charge transport by fluctuations of the intermolecular coupling has been theoretically studied and calculated recently [65, 66]. It is shown that dynamic (thermal) disorder is able to localize charge carriers efficiently. The influence of molecular thermal motion (and static disorder)
on the energetic distribution of states is also covered by the polarization theory [2], since small changes of the molecular arrangement result in an altered polarizability and thus additional energy levels. In terms of electron-phonon interactions, molecular motions play an important role in the framework of an extended Holstein model [7].

By the comparison of rubrene and a derivative, the influence of the crystal structure on the charge carrier mobility was investigated. Single crystals of a new rubrene derivative (5,11-BTBR) have been grown and the semiconducting polymorph 2 has been electrically characterized. The trap density in the energy gap is of order $10^{15}$ cm$^{-3}$ eV$^{-1}$; low enough to reveal band-tail like states with a characteristic energy of 22 meV. This low DOS and the occurrence of narrow band tails are characteristic for high-quality organic crystals. Presumably having a similar crystal structure and in-plane arrangement of the molecules compared with rubrene, 5,11-BTBR (2) has shown a comparably high in-plane field-effect mobility of up to 12 cm$^2$/Vs (on an OTS-treated SiO$_2$ gate insulator). It fits into the present understanding of the relation between structure and mobility as well that the in-plane mobility in 5,11-BTBR in its other polymorphic form (1) is too low to be measured because the tetracene backbones are twice as wide apart from each other compared with rubrene, and π-stacking of the backbones is absent. In order to get a better understanding of the relationship between crystal structure and charge transport, the full structure of 5,11-BTBR (2) and, based thereon, band structure calculations are needed. Additionally, several other new modifications of rubrene are subjects of the ongoing research.

Finally, we reported on in situ structural and conductivity studies of pentacene intercalation, in both thin films and single crystals. This enabled us to address the intercalation dynamics, staging issues, and the structural intercalation phase diagram. For iodine-doped pentacene, we find that both thin films and single crystals intercalate easily, and are only found in an effectively metallic stage-1 structure across the whole temperature–iodine partial pressure phase diagram that was assessed. Due to the insertion of the I$_3^-$ ions between the molecular layers, the system becomes strongly 2-dimensional, as reflected in the huge anisotropy in the resistivity in and perpendicular to the layers of $>10^7$. For pentacene thin films, we find that successive intercalation and desorption induces an irreversible and controlled change in the polymorph of the crystal structure. Intercalated single crystals show a quasi-metallic behavior of the conductivity as well, although their structural degradation due to the iodine intercalation, as monitored by the width of the rocking curve, is much more pronounced compared to thin films. From Hall measurements in a thin film, we derive a hole mobility of 0.4 cm$^2$/Vs and a concentration of free carriers of $1 \times 10^{21}$ cm$^{-3}$ for an intercalated thin film with an estimated stoichiometry of (PEN)$_2$I$_2$.

To conclude, the road to organic molecular crystals and devices with high mobilities and
low trap densities is not only hampered by extrinsic factors such as process-induced defects, but also intrinsically due to the effects arising from the weak intermolecular interactions, as expressed in large thermal motions: small effective band widths, strong trend to charge carrier localization by polarization and due to electron-phonon coupling. However, there are many tuning possibilities due to the infinite choice of materials.
References


REFERENCES


[40] T. Siegrist, private communication.


Soc. 126, 11168 (2004).


50, 3462 (1994).


[93] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum,


Curriculum Vitae

May 5\textsuperscript{th} 1974  Born in Altdorf UR (Switzerland)

1981 – 1987  Primary school in Flüelen UR

1987 – 1994  Kantonale Mittelschule Uri, Altdorf (Matura Typus A)

1994 – 2000  Student at the ETH Zürich, faculty of chemistry
(“Interdisziplinäre Naturwissenschaften”)

October 1999 – March 2000  Diploma thesis “Erste Schritte auf dem Weg zur spannungs-
kontrollierten magnetischen Kopplung” in the group of Prof. H.C. Siegmann, under guidance of Prof. M. Landolt.

March 2000  Graduation from ETH Zürich. Degree: Dipl. Natw. ETH

April – December 2000  Scientific and teaching assistant in the group of Prof. H.C. Siegmann / Prof. D. Pescia, under guidance of Prof. M. Landolt. Cooperation with PD R. Allenspach from IBM Research Laboratory in Rüschlikon ZH.

2001 – 2006  Ph.D. student and teaching assistant in the group of Prof. B. Batlogg at ETH Zürich.
Dank

Jede Dissertation in experimenteller Physik ist nicht ausschliesslich das Werk eines Doktoranden, sondern kommt erst durch die Zusammenarbeit innerhalb und ausserhalb einer Forschungsgruppe zustande.


Prof. J. Fröhlich möchte ich für den angenehmen Prüfungsvorsitz danken.

Spezieller Dank gebühr den Mitgliedern der Gruppe Batlogg, sowohl für den technisch-wissenschaftlichen Support als auch die persönlich guten Beziehungen:


Bei zahlreichen Wanderungen und Bergtouren war Benjamin Rössner mit Begeisterung dabei. Sein breites Wissen in beinahe allen Gebieten beeindruckt, so auch bei den regelmässigen wissenschaftlichen Diskussionen.

Markus Brühwiler ist mit mir durch gute und schlechte (wissenschaftliche) Zeiten gegangen. Bei unserem TransSwissTrail-Projekt sind wir zwar nicht bis Chiasso gekommen, aber zahlreiche andere Wanderungen waren vom Gipfelerlebnis gekrönt.

Mit Peter Geiser um Mitternacht im Kaffeeraum zu diskutieren war immer sehr lehrreich
und anregend. Die gemeinsame Besteigung des Schilthorns wird wohl allen Beteiligten noch lange im Gedächtnis bleiben.


Wolfgang Kalb als Amtsjüngster der Doktoranden hat gerne zugehört, um das gesammelte Wissen zu übernehmen, und durch seine kritischen, fundierten Fragen zum Fortschritt beigetragen. Für die Fortsetzung und den Abschluss seiner Dissertation wünsche ich ihm alles Gute!


David Gundlach brought new enthusiasm, his experience and the American way of life and research into our lab. Sorry, Dave, that I did not listen always to your suggestions on experiments and working hours (after all, no girlfriend was preventing me from being in the lab...)


Jun Takeya and Tatsuo Hasegawa were paragons of sedulity. Their presence and their scientific work enriched the group. Furthermore, they showed a good kind of humor that was in contrast to their traditional Japanese reserve.

Götz Schuck ist mir mit Rat und Tat zur Seite gestanden, wenn’s ums Lösen diverser Kristallstrukturen ging.

Unsere Techniker, Kurt Mattenberger und Hanspeter Staub, waren dafür besorgt, dass die Apparaturen meist einwandfrei funktioniert und damit die Messungen ermöglicht haben. Daneben war es interessant, mit ihnen über Musik, Politik und Bergtouren zu sprechen.

Unsere Sekretärin, Gaby Strahm, war immer sehr hilfsbereit und ihre Einladungen zum
Apéro stets sehr willkommen.

Daneben haben zahlreiche Semester- und DiplomstudentInnen die Gruppe bereichert.


Eine Bereicherung waren die Gespräche mit den übrigen Mitgliedern der Hochdruck- und Spektroskopie-Gruppe, so z.B. die Einführung in die Kunst der Wodka-Kultur durch Andrey, die Diskussionen über Geigerinnen und Geiger mit Kris und die Kaffeerunde mit Michela, Andrea und Florian.

Ein grosser Dank geburt zuletzt meinen Eltern, der übrigen Familie sowie zahlreichen Kolleginnen und Freunden für die grosse Unterstützung.