

Linköping Studies in Science and Technology

Dissertation No. 1317

# Development of Organic-Based Thin Film Magnets for Spintronics

Elin Carlegrim



**Linköpings universitet**  
**INSTITUTE OF TECHNOLOGY**

Department of Physics, Chemistry and Biology  
Linköping University, SE-581 83 Linköping, Sweden

Linköping 2010

ISBN: 978-91-7393-385-8

ISSN: 0345-7524

Copyright © Elin Carlegrim, 2010, unless otherwise noted

Printed by LiU-Tryck, Linköping, Sweden, 2010

# Abstract

---

In the growing field of spintronics, development of semiconducting magnets is a high priority. Organic-based molecular magnets are attractive candidates since their properties can be tailor-made by organic chemistry. Other advantages include low weight and low temperature processing. Vanadium tetracyanoethylene,  $V(TCNE)_x$ ,  $x \sim 2$ , is particularly interesting since it is one of very few semiconducting magnets with magnetic ordering above room temperature.

The aim of the research presented in this thesis was to prepare and characterize thin film organic-based magnets with focus on  $V(TCNE)_x$ . Photoelectron and absorption spectroscopy studies were performed leading to a more complete picture of the electronic and chemical structure of the material. Depending on the preparation method of  $V(TCNE)_x$ , the material contains varying amounts of disorder which among other things makes it very air sensitive. In this thesis, a new preparation method for organic-based magnets based on physical vapor deposition is presented and the first result shows that it generates less air sensitive  $V(TCNE)_x$  than previous methods reported. A new spin valve design based on  $V(TCNE)_x$  was proposed where the material delivers both spin-filtering and spin-transporting functionality, making use of its fully spin-polarized transport levels. In such devices, the interface of  $V(TCNE)_x$  with ferromagnetic metals is of great importance and was hence studied. As vanadium ions always are very reactive towards oxygen, substituting vanadium by a less reactive ion would be desirable from both an interface engineering and device packaging perspective. Very few alternatives exist however that orders magnetically above room temperature. In order to find out what are the key design criteria for preparing thin film semiconducting room temperature magnets, we have begun to study systems which order magnetically much below room temperature and compared them with  $V(TCNE)_x$ .



# Populärvetenskaplig sammanfattning

---

I mitten av 1980-talet började forskare studera magneter baserade på organiska material. Vanadin tetracyanoetylen är ett av de mest uppmärksammade materialen eftersom det är magnetiskt i rumstemperatur samt halvledande. Fördelen med magneter baserade på organiska material jämfört med konventionella magneter av metall är att deras egenskaper kan skraddarsys med hjälp av organisk kemi. Möjliga användningsområden för dessa material finns bl.a. inom framtidens elektronik, s.k. spinntronik, där inte bara elektronens laddning utan även dess spinn (rotation kring den egna axeln) kan användas för att lagra information. Spinntronik baserad på metall finns redan i dag i varje hårddisk och uppmärksammades med Nobelpriset 2007.

Syftet med forskningen som presenteras i denna avhandling var att tillverka och studera tunna filmer av vanadin tetracyanoetylen. Innan organiska magneter kan realiseras i komponenter är det viktigt att få mera kunskap om materialens uppbyggnad och därför har vanadin tetracyanoetylen karakteriserats med olika typer av fotoelektron-spektroskopi och absorptionspektroskopi. Beroende på vilken tillverkningsmetod som materialet framställts med så innehåller det olika grader av strukturella defekter vilket bl.a. leder till att det blir mycket luftkänsligt och oxideras. I denna avhandling presenteras en ny tillverkningsmetod och de första resultaten tyder på att vanadin tetracyanoetylen tillverkat med denna metod blir mera beständigt mot syre. Vidare föreslås en ny design av en spinntronikkomponent (s.k. spinnventil) som är baserad på denna magnet. Dessa komponenter innehåller metall och därför är gränssnittet mellan vanadin tetracyanoetylen och metall viktigt och studerades med ovan nämnda metoder. Vanadin är mycket reaktivt med syre och därför är det önskvärt att byta ut det mot en mindre reaktiv metall, dock finns det få alternativ som ger material som är magnetiska i rumstemperatur. För att finna de designkriterier som ger material som är magnetiska vid rumstemperatur har vi genomfört studier på liknande material som endast är magnetiska vid mycket lägre temperaturer och jämfört dem med vanadin tetracyanoetylen.



# Preface

---

With this thesis I am summarizing the main part of the work I have done as a PhD student in the Division of Surface Physics and Chemistry at the Department of Physics, Chemistry and Biology at Linköping University. The thesis is a development of my Licentiate thesis\* and as such large parts of the introductory section are mainly taken directly from the Licentiate work.

The study concerns organic-based molecular magnets which is a new research area, considered as basic science. It has therefore been very interesting to be part of preparation process development and characterization of organic-based magnets. The aim of this thesis was to obtain knowledge about a particular organic-based magnet which is appealing for use in spintronic devices.

I have learnt a lot about vacuum systems and advanced spectroscopy techniques. The laboratory work has been carried out at our home-lab in Linköping as well at the synchrotron radiation facility in MAX-lab, Lund, Sweden. Together with colleagues I have developed one of the methods for preparation of thin films of organic-based molecular magnets. This process was patented and I was involved both in the financial support applications and in the writing process, from application to final patent.†

I have very much appreciated to be a member in an international group, meeting people from different parts of the world. I have also had the opportunity to attend several international conferences and summer schools, presenting some of the research, for example at the Materials Research Society (MRS) fall meeting in Boston, 2006.

*Elin Carlegrim*

Linköping, April 2010

---

\* Preparation and Characterization of an Organic-Based Magnet, Licentiate Thesis 1338, Elin Carlegrim, Linköping University, 2007.

† Process of producing organomagnetic materials, M. Fahlman, E. Carlegrim, A. Kancierzewska and P. Bhatt, SE0702226.



# Acknowledgements

---

This thesis would not have been realized without help and support from a number of people and therefore I would like to thank:

- First of all, my supervisor Prof. **Mats Fahlman** for guidance, support and for introducing me to the field of organic-based magnets and photoelectron spectroscopy.
- All the members, past and present, of the Division of Surface Physics and Chemistry for discussions and for help with lab equipment, but also for lunch and coffee break discussions concerning other topics than research. Especially, I would like to thank the people that have contributed to the included papers in this thesis. I am also grateful to **Linda Lindell** for all support in the end my PhD studies.
- My friends outside university, for sharing small and big things in life. Particularly, I would like to mention **Anna S**, **Maria** and my sisters, **Anna** and **Sara**.
- My parents, **Ingrid** and **Börje** for support and interest in what I am doing.

Last, but not least, **Anders**, **Elsa** and the fourth family member on its way for reminding me everyday of what is most important in life.



# Papers Included in the Thesis

---

## Paper I

**Near-edge x-ray absorption studies of Na-doped tetracyanoethylene films: A model system for the  $V(\text{TCNE})_x$  room-temperature molecular magnet**

E. Carlegrim, B. Gao, A. Kanciurzevska, M.P. de Jong, Z. Wu, Y. Luo and M. Fahlman

*Physical Review B* **77**, 054420 (2008)

## Paper II

**The unoccupied electronic structure of the semi-conducting room temperature molecular magnet  $V(\text{TCNE})_2$**

E. Carlegrim, A. Kanciurzevska, M.P. de Jong, C. Tengstedt and M. Fahlman

*Chemical Physics Letters* **452**, 173 (2008)

## Paper III

**Air-stable organic-based semiconducting room temperature thin film magnet for spintronics applications**

E. Carlegrim, A. Kanciurzevska, P. Nordblad and M. Fahlman

*Applied Physics Letters* **92**, 163308 (2008)

## Paper IV

**Characterization of the  $Ni/V(\text{TCNE})_x$  interface for hybrid spintronics applications**

E. Carlegrim, Y. Zhan, F. Li, X. Liu and M. Fahlman

*Organic Electronics, in press*

## Paper V

**Electronic structure of thin film cobalt tetracyanoethylene,  $\text{Co}(\text{TCNE})_x$**

E. Carlegrim, Y. Zhan, M.P. de Jong and M. Fahlman

*In manuscript*



# The Author's Contribution to the Papers

---

## Paper I

All the experimental work and data analysis in cooperation. Wrote the first draft and was responsible for the iterative process to the final version. The theoretical work was performed by collaborators at KTH, Stockholm.

## Paper II

All the experimental work and data analysis in cooperation. Wrote the first draft and was responsible for the iterative process to the final version.

## Paper III

Development of the new preparation method, photoelectron spectroscopy studies and data analysis in cooperation. Wrote the first draft and was responsible for the iterative process to the final version. The SQUID measurements were performed by P. Nordblad at Uppsala University.

## Paper IV

Major part of the experimental work and all of the data analysis. Wrote the first draft and was responsible for the iterative process to the final version.

## Paper V

All the experimental work and data analysis. Wrote the first draft and was responsible for the iterative process to the final version.



## Related Papers not Included in the Thesis

---

### **Photoelectron spectroscopy of the contact between the cathode and the active layers in plastic solar cells: the role of LiF**

S.K.M. Jönsson, E. Carlegrim, F. Zhang, W.R. Salaneck and M. Fahlman  
*Japanese Journal of Applied Physics* **44**, 3695 (2005)

### **X-ray magnetic circular dichroism and resonant photoemission of V(TCNE)<sub>x</sub> hybrid magnets**

C. Tengstedt, M.P. de Jong, A. Kanciurzevska, E. Carlegrim and M. Fahlman  
*Physical Review Letters* **96**, 057209 (2006)

### **Chemical bonding in V(TCNE)<sub>x</sub> (x~2) thin-film magnets grown *in situ***

M.P. de Jong, C. Tengstedt, A. Kanciurzevska, E. Carlegrim, W.R. Salaneck and M. Fahlman  
*Physical Review B* **75**, 64407 (2007)

### **Study on Poly(3,4-ethylene dioxythiophene)-Poly(styrenesulfonate) as a plastic counter electrode in dye sensitized solar cells**

A. Kanciurzevska, E. Dobruchowska, A. Baranzahi, E. Carlegrim, M. Fahlman and M.A. Gîrțu  
*Journal of Optoelectronics and Advanced Materials* **9**, 1052 (2007)

### **Process of producing organomagnetic materials**

M. Fahlman, E. Carlegrim, A. Kanciurzevska and P. Bhatt  
Patent number: SE0702226 (2007)

### **Electronic structure of thin film iron-tetracyanoethylene: Fe(TCNE)<sub>x</sub>**

P. Bhatt, E. Carlegrim, A. Kanciurzevska, M.P. de Jong and M. Fahlman  
*Applied Physics A* **95**, 131 (2009)

**Ferromagnetism above room temperature in nickel-tetracyanoethylene thin films**

P. Bhatt, A. Kanciurzevska, E. Carlegrim, M. Kapilashrami, L. Belova, K.V. Rao and M. Fahlman

*Journal of Materials Chemistry* **19**, 6610 (2009)

**The role of aluminium oxide buffer layer in organic spin-valves performance**

Y.Q. Zhan, X.J. Liu, E. Carlegrim, F.H. Li, I. Bergenti, P. Graziosi, V. Dediu, and M. Fahlman

*Applied Physics Letters* **94**, 053301 (2009)

**Efficient spin injection through exchange coupling at organic semiconductor/ferromagnet heterojunctions**

Y. Zhan, E. Holmström, R. Lizárraga, O. Eriksson, X. Liu, F. Li, E. Carlegrim, S. Stafström, and M. Fahlman

*Advanced Materials* **21**, 1 (2009)

**Experimental evidence for ferromagnetism at room-temperature in MgO thin films**

M. Kapilashrami, J. Xu, K.V. Rao, L. Belova, E. Carlegrim and M. Fahlman

*Submitted*

# Contents

---

<b>1</b>	<b>Introduction</b>	<b>1</b>
<b>2</b>	<b>Organic-Based Magnets</b>	<b>3</b>
2.1	Origin of Magnetic Ordering and Interactions	3
2.1.1	<i>Magnetic Ordering</i>	4
2.1.2	<i>Magnetic Interactions</i>	5
2.1.3	<i>Factors Influencing Magnetic Ordering</i>	5
2.1.4	<i>Definitions of Some Key Parameters in Magnetism</i>	6
2.2	Materials	6
2.3	Spintronics	9
<b>3</b>	<b>Preparation Methods</b>	<b>13</b>
3.1	Solution-Based Preparation	13
3.2	Chemical Vapor Deposition (CVD)	14
3.3	Physical Vapor Deposition (PVD)	15
<b>4</b>	<b>Experimental Techniques</b>	<b>17</b>
4.1	Photoelectron Spectroscopy	17
4.1.1	<i>The Principle of Photoionization</i>	17
4.1.2	<i>Core Level Spectroscopy (XPS)</i>	19
4.1.3	<i>Valence Level Spectroscopy (UPS)</i>	21
4.1.4	<i>Reference Level</i>	22
4.1.5	<i>Intensity and Resolution</i>	23
4.2	Photon Sources	23
4.3	Absorption Spectroscopy	24
4.4	Resonant Photoelectron Spectroscopy (RPES)	26
4.5	Superconducting Quantum Interference Device (SQUID)	26
<b>5</b>	<b>Equipment</b>	<b>29</b>
5.1	Moses	29
5.2	Scienta	30
5.3	Beamline I311	31
5.4	Beamline D1011	32

**6 Summary and Future Outlook** **35**

---

6.1 Background 35

6.2 Summary of the Thesis 36

6.3 Current Studies 41

6.4 Future Outlook 41

**References** **43**

---

**Paper I**

**Paper II**

**Paper III**

**Paper IV**

**Paper V**

# 1 Introduction

---

Magnets based on organic materials, so-called organic-based molecular magnets (OMMs), is a new and ‘exotic’ field of organic electronics<sup>1</sup>. In contrast to conventional atom-based transition- and rare-earth-based metallic magnets, the basis in organic-based magnets is molecules. The main advantage of these magnets is that their magnetic and electronic properties can be tuned by molecular design. Other advantages include conductivity ranging from semi-conducting to insulating, low weight, low temperature processing, low environmental contamination etc.<sup>2, 3</sup> Some organic-based magnets also offer properties not seen in conventional magnets, such as light-induced magnetism, solubility in organic solvents and biocompatibility.<sup>2-5</sup> The belief in that organic magnets could exist was of theoretical nature, formulated in the 1950s, but it took until the mid 1980s until the first organic-based magnets were prepared.<sup>6</sup> A breakthrough came 1991 when the first room temperature organic-based magnet was discovered,<sup>7</sup> opening the door to many potential applications. In the same year also the first purely organic magnets were discovered.<sup>8, 9</sup> Once those materials are well characterized, they may very well be used in both traditional applications and prospective applications not thought of yet. Room temperature organic-based magnets could eventually be used as functional coatings, for example frequency or magnetic shielding and anti-static coatings.<sup>10</sup> One can also imagine less traditional applications in so-called spin-based electronics<sup>11</sup> (spintronics), such as memory devices, sensors, medicine carriers etc. However, before this can be reality, deeper understanding in the physical and chemical properties of the materials is required. Different electron spectroscopy techniques, e.g. photoelectron spectroscopy (PES) and near edge X-ray absorption fine structure (NEXAFS) spectroscopy, are well suited for characterization of the surfaces and interfaces of the materials as the energy of photoexcited electrons give

information regarding the electronic structure as well as chemical composition and environment.

This thesis consists of an introductory part and a set of five included papers. The introductory part provides an overview of organic-based molecular magnets, their preparation methods, some of the experimental techniques used for studying OMMs and a presentation of the equipment which have been utilized in this work. Finally the work in this thesis is summarized and a future outlook is given. Hence, the aim of the introductory part is to give a brief overview of the subject, while the included papers reflect my contribution to the research field.

## 2 Organic-Based Magnets

---

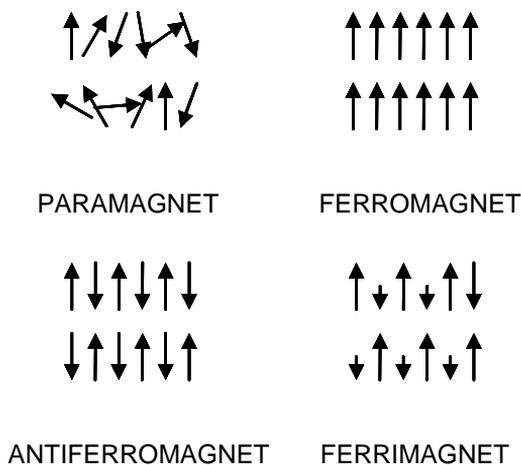
In contrast to conventional atom-based magnets, which are based on transition- or rare-earth metals with net spin in d- or f-orbitals, organic-based magnets have net spins residing in p- or s-orbitals. Organic-based magnets can be classified into two groups, purely organic or hybrid organic-inorganic. In the hybrid organic-inorganic magnets, the organic part can be either passive, (without net spin) or active (with net spin). Further, they can be divided into groups depending on the number of metal ions, type of ligands and their lattice dimension, i.e. isolated molecules (0D), chain (1D), layer (2D) or bulk networks (3D), etc.<sup>2</sup> One of the most extensively studied family of 3D organic-based magnets is transition-metal tetracyanoethylene complexes,  $M(\text{TCNE})_x$ .<sup>7, 12-14</sup> The large interest in these magnets started with vanadium tetracyanoethylene,  $V(\text{TCNE})_x$ , which was the first organic-based magnet to show magnetic ordering above room temperature.<sup>7</sup> Since the main focus in this thesis is  $V(\text{TCNE})_x$ , its properties and potential applications are discussed in this chapter, after a short introduction to magnetism.

### 2.1 Origin of Magnetic Ordering and Interactions

The essential component of a magnetic material is the existence of un-paired electrons, or more precisely spins associated with un-paired electrons (a net spin). Magnetic ordering is a cooperative effect and these spins have to interact with each other in order to create a magnetic material. This ordering effect of interaction has to be larger than the disordering effect of thermal agitation. Hence, magnetic ordering only occurs below a critical temperature, the so-called Curie temperature of ferro- and ferrimagnets or Néel temperature of antiferromagnets.<sup>15, 16</sup>

### 2.1.1 Magnetic Ordering

The interaction of spins at nearby sites leads to different spin configurations, namely, para-, ferro-, antiferro- and ferrimagnetism.<sup>17</sup> In a paramagnet the spins are aligned in different directions and those directions change rapidly with respect to time, even at low temperatures. If an external field is applied, the spins (may) align in the same direction. Besides, all ferro- antiferro- and ferrimagnetic materials become paramagnetic above their critical temperature. A ferromagnet has a spontaneous magnetization (net spin) even in absence of an external magnetic field since the spins are aligned in the same direction below the Curie temperature. In an antiferromagnetic material the spins are aligned anti-parallel to each other, leading to a zero net spin.



**Figure 2.1** Examples of different spin configurations in absence of an external field, see e.g. *Introduction to Solid State Physics* by C. Kittel.<sup>17</sup>

Ferrimagnetism is a special case of antiferromagnetism and below their critical temperature these materials have a net magnetic moment. Therefore, ferrimagnets behave like ferromagnets at the macroscopic scale. It is important to note that those behaviors discussed above are not a property of an individual molecule, they are bulk properties.

### 2.1.2 Magnetic Interactions

The main type of magnetic interaction is the Heisenberg exchange interaction.<sup>2, 3</sup> The Heisenberg effect is a quantum effect and is mainly due to the Pauli's exclusion principle. Other types of magnetic interactions (e.g. dipole interaction) are generally neglected.<sup>3</sup> The pair-wise spin interaction in (ferro- and antiferro-) magnetic systems at a zero applied magnetic field may be described by the Heisenberg Hamiltonian:

$$H = -2 \sum_{i,j} J_{i,j} S_i \cdot S_j \quad (2.1)$$

where  $i$  and  $j$  are independent of directions (x, y or z) of the nearest-neighbor sites and  $S_i \cdot S_j$  is the scalar product of these adjacent vector spins.  $J_{i,j}$  is the exchange constant (ferromagnetic,  $J > 0$ , or antiferromagnetic,  $J < 0$ ), summing over all possible interactions. However, this is a basic picture and further contributions can be accounted for and added to the equation.<sup>2, 18</sup> Since organic-based magnets often are disordered, a term representing random magnetic anisotropy (see paragraph below) is sometimes included into the equation:

$$H = -2 \sum_{i,j} J_{i,j} S_i \cdot S_j - D_r \sum_i (\mathbf{n}_i \cdot S_i)^2 \quad (2.2)$$

where  $D_r$  is a measure of the random anisotropy strength and  $\mathbf{n}_i$  is a unit vector that corresponds to a random field, pointing in the direction of local anisotropy.<sup>2</sup>

### 2.1.3 Factors Influencing Magnetic Ordering

The main factors influencing the magnetic ordering are spin dimensionality, lattice dimensionality, spin value but also disorder and frustration.<sup>18</sup> An example of disorder frequently occurring in magnetic amorphous solids (e.g. hybrid organic-inorganic compounds) is random magnetic anisotropy,<sup>19</sup> i.e. different magnetic interaction in different directions. Frustration is another phenomenon typical of organic-based magnets, where a spin system cannot minimize the energy of each spin pair in a network, simultaneously.<sup>18</sup> This leads to peculiar magnetic phenomena

at low temperatures, e.g. spin glass state,<sup>2, 3</sup> since the direction of the spins locally freezes and changes their orientation extremely slowly with respect to time below a certain temperature.<sup>14</sup> Spin glass behavior is commonly occurring for organic-based magnets, e.g. V(TCNE)<sub>x</sub> powder magnets (see chapter 3).

### 2.1.4 Definitions of Some Key Parameters in Magnetism

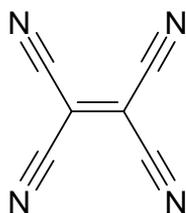
Susceptibility, coercivity and remanence are three important parameters when describing the magnetization of a material. The susceptibility is used to describe the response of a material to an applied field. The coercivity describes the required intensity of an applied magnetic field to completely demagnetize a magnetic material which has been magnetized to saturation. When the coercive field of a magnet is large, the material is said to be hard (permanent magnets), while if the coercive field is low, the magnet is known to be soft. The remanence is a measure of the magnetization of a magnetic material after an external field has been removed. Both the coercivity and remanence can be illustrated by a so-called hysteresis curve.<sup>16</sup>

## 2.2 Materials

M(TCNE)<sub>x</sub>, where M = V, Fe, Mn, Co, Ni etc., TCNE = tetracyanoethylene,  $x \sim 2$ ,<sup>7, 12-14, 20</sup> is one of the most studied families of organic-based magnets. Recently, it has been extended to also include Cr, Nb and Mo.<sup>21</sup> An unlimited number of variants of M(organic molecule)<sub>x</sub> can be prepared by exchanging the metal, or the organic molecule,<sup>22-24</sup> as well as both. Combination of metals, i.e. M'<sub>z</sub>M''<sub>1-z</sub>(TCNE)<sub>x</sub>,  $0 < z < 1$ , has also been reported,<sup>25-27</sup> some of them showing Curie temperatures above room temperature. Moreover, the stoichiometry of the species in M(TCNE)<sub>x</sub> can be varied, such that x deviates from 2, while still obtaining magnetic ordering above room temperature.<sup>28</sup> However, if this is correct or if the room temperature magnetic ordering in those M(TCNE)<sub>x</sub> magnets are due to other factors are still under debate.<sup>29, 30</sup>

Particularly V(TCNE)<sub>x</sub> has caught the interest since it was the first room temperature ( $T_C$  is close to 400 K) organic-based magnet when reported in 1991.<sup>7</sup> Unfortunately, the material is extremely air sensitive and this, together with its disordered structure, has hindered and delayed studies of the material. The magnet

can be prepared either as a powder or as a thin film (see chapter 3), leading to slightly different properties. In the discussion below, thin films are considered.



(a)

M	T <sub>C</sub> (K)
V	370
Fe	95
Mn	75
Co	40
Ni	40

(b)

**Figure 2.2** (a) The chemical structure of TCNE. (b) Curie temperatures of different  $M(\text{TCNE})_x$ <sup>7, 12-14, 26</sup> (the values are approximate and are derived from the powder form of the materials).

In  $\text{V}(\text{TCNE})_x$ , each vanadium ion is coordinated to six nitrogen atoms most likely in a slightly distorted octahedral environment. The TCNE molecules are planar or twisted and can bind to up to four vanadium ions. The local environment is well-defined with a small distribution of V-N bond lengths, having an average distance of 2.084(5) Å in room temperature. The strong (covalently) bonded 3D network explains the insoluble nature of the compound.<sup>31</sup>

There is an extensive activity in developing new materials for spintronics, but so far very few show room temperature ordering and semiconducting behavior.<sup>32</sup>  $\text{V}(\text{TCNE})_x$  is a semiconductor with a conductivity of about  $10^{-4} \text{ Scm}^{-1}$  at room temperature. It decreases with decreasing temperature, which suggests a hopping transport mechanism.<sup>33</sup> A low coercive field of about 4.5 Oe has been reported at room temperature, which is characteristic of a soft magnet.<sup>34</sup>

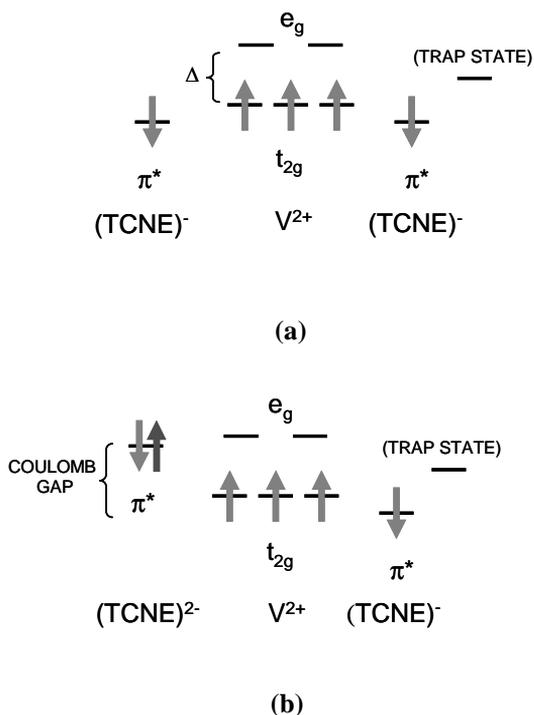
The coupling between the 3/2 spin on  $\text{V}^{2+}$  and 1/2 spin on the two TCNE<sup>-</sup> species is proposed to be antiferromagnetic, yielding a ferrimagnetic state and hence a net spin of 1/2 for each  $\text{V}(\text{TCNE})_2$  unit.<sup>35</sup> Magnetotransport measurement of  $\text{V}(\text{TCNE})_x$  thin films have demonstrated positive magnetoresistance,<sup>32, 33</sup> i.e. increase in resistance with applied field. This anomalously large magnetoresistance

was explained by a model where the  $\pi^*$ -band is split into two sub-bands, one occupied and one unoccupied, with opposite spin polarization. From this model it is proposed that  $V(\text{TCNE})_x$  can be described as a fully spin-polarized, semiconductor.<sup>33</sup> No experimental evidence for the proposed valence electronic structure existed, however. This assumption was later modified after experimentally showing that the highest occupied molecular orbital (HOMO) actually is  $V(3d)$ -derived (as described above) and hence not  $\text{TCNE}^-$ -derived.<sup>36</sup> In this modified model of the ground state of  $V(\text{TCNE})_2$ , the  $V(3d)$  is proposed to split into two orbitals,  $e_g$  and  $t_{2g}$ , due to crystal field splitting,  $\Delta$ , a well-known property of 3d elements. The HOMO is mainly localized on the  $V(3d)$  units and is characterized by strong hybridization between  $V(3d)$  and the  $\text{TCNE}^-$  units.<sup>36, 37</sup> The experimental result of the lowest unoccupied molecular orbital (LUMO) of  $V(\text{TCNE})_x$  was in agreement with the one stated above as it is mainly located on the  $\text{TCNE}^-$  units (see **Paper I** and **Paper II**). It is important to note that there may be trap states present, depending on the preparation method. Those trap states are located below the  $\text{TCNE}^{2-}$  level (see **Paper II**).

In devices, charges are injected into the material and when adding an extra electron to a small system, such as  $V(\text{TCNE})_x$ , a Coulomb gap around the Fermi level is created (see Fig. 2.3).<sup>38</sup> In larger systems, such as polymers, the added charges are allowed to rearrange and distribute over a large area instead of creating a Coulomb gap.

Calculations of  $V(\text{TCNE})_x$  have shown that the vanadium-cyano bonds are characterized by a large crystal field parameter,  $10Dq=2.3$  eV, and strong ligand to metal charge transfer effects.<sup>37</sup> The electronic structure of some other members in the  $M(\text{TCNE})_x$  family has also been studied<sup>30, 39</sup> (see also **Paper V**). Those studies indicate a completely different electronic structure and weaker metal-TCNE ligand interaction as compared to  $V(\text{TCNE})_x$ .<sup>37</sup>

In summary, the room temperature magnetic ordering in combination with semiconducting and spin-polarized transport properties makes  $V(\text{TCNE})_x$  very attractive for spintronic applications, see paragraph, below.



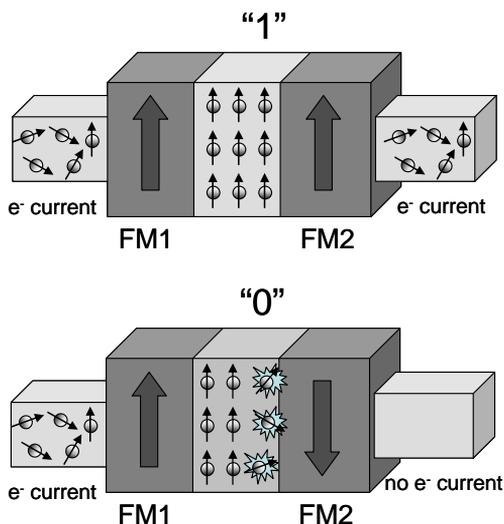
**Figure 2.3** Frontier electronic structure of  $V(TCNE)_2$ . For more details, see **Paper II (a)** Ground state. **(b)**  $V(TCNE)_x$  with one extra electron added. Copyright © Elsevier B.V.

## 2.3 Spintronics

In the beginning, organic-based magnets were thought of as replacement of traditional magnets in generators, motors, transformers etc. More recently it was shown that they are unlikely to compete with metal magnets.<sup>2</sup> Instead, they may find their own niches since they have exposed properties never associated with magnets before,<sup>2, 4</sup> such as bistability (e.g. light-induced magnetism), transparency, solubility in organic solvents and potentially biocompatibility. The most promising applications based on organic-based magnets may be found in the growing field spintronics.<sup>40, 41</sup> Spintronic devices utilize not only the charge of the electron as information carrier, but also its spin direction. Advantages of using the electron spin as information carrier include, faster data processing speeds, non-volatility and less electrical power consumption.<sup>41</sup> Examples of (potential) spintronic devices are spin-

valves, spin-based light-emitting diodes and spin-based field effect transistors etc.<sup>40</sup>

<sup>41</sup> To date, the most successful spintronic device is the spin valve.



**Figure 2.4** The principle of a spin valve. Low resistance represents “1” and high resistance represents “0”, respectively. The external magnetic field is denoted by the large arrows. The spacer (light grey) is sandwiched between two ferromagnetic (FM) materials, one with fixed magnetization (FM1) and one with tunable magnetization (FM2). The figure is based on an illustration from the magazine *Ny Teknik*.<sup>42</sup>

The principle of a spin valve is that a thin layer of a non-magnetic material is spaced between two layers of ferromagnetic metal.<sup>43</sup> One of the two magnetic layers has fixed magnetization (a hard magnet), whereas the other magnetic layer (a soft magnet) can be tuned by a weak external field. The spacer material should be reasonable conductive and have long spin-coherence length. Hence, the magnetization of such a device can be changed, giving high resistance or low resistance, simulating a bit, “1” or “0”. The spin valve structure is the basis of the discovery of the giant magnetoresistance (GMR) effect by Albert Fert and Peter Grünberg, for which they were rewarded the Nobel prize 2007.<sup>44</sup> Inorganic spintronic devices, read heads for hard disk drivers, can nowadays be found in every computer.

It has been suggested that combining the advantages of spintronics with the advantages of organic electronics would lead to future's spintronic devices.<sup>11, 45</sup> Organic materials exhibit advantages, such as mechanically flexibility, low temperature and potential low-cost device fabrication, tunability of the properties via chemical routes etc.<sup>1</sup> In addition, light elements have weak spin-orbit coupling and low hyperfine interaction, leading to longer spin-coherence times as compared to inorganic materials.<sup>46</sup> The first organic-based spintronic device was presented in 1998<sup>47</sup> but so far no “all-organic” spintronic device has been reported. Challenges in the field of organic spintronics include, control and understanding of the transport mechanism and of the interfaces, development of materials with higher Curie temperature and higher mobility as well as with increasing sensitivity to weak magnetic fields.

$V(\text{TCNE})_x$  has been proposed to be used in a hybrid spin valve design (see Fig. 2.4) as the soft magnetic layer.<sup>48</sup> In addition, we have recently proposed a new spin design based on  $V(\text{TCNE})_x$  where it is sandwiched *in between* the two ferromagnetic layers, making use of its fully spin-polarized transport levels (see **Paper IV**).



## 3 Preparation Methods

---

Fabrication of conventional transition metal and rare earth based magnets requires high temperature metallurgical synthesis methodologies and is very energy consuming. Organic-based molecular magnets (OMMs) have the advantage of low-cost organic synthetic methodologies and together with the concept of “designer magnets”,<sup>49</sup> which refers to that their properties can be tailor-made, make them attractive in future generations of electronic, magnetic and photonic devices. However, OMMs have shown to be complicated to prepare and reproduction of the materials have sometimes shown to be unpredictable.<sup>3</sup> Depending on preparation method, different amounts of disorder are introduced in the material, which can worsen its properties.<sup>34</sup> Hence, it is of high importance with further improvements of the preparation methods.

In this chapter the development and the preparation routes of the magnets in the  $M(\text{TCNE})_x$  family are discussed with focus on preparation of  $V(\text{TCNE})_x$ .

### 3.1 Solution-Based Preparation

The first and most frequently used method for preparation of all organic-based magnets is solution-based organic synthesis preparation. The source materials, the so-called precursors, are allowed to react in an organic solvent. The solvent can be either coordinating, which means that the vanadium ions are being blocked by solvent molecules from binding to the nitrogen of the TCNE molecules or non-coordinating.<sup>34, 50</sup> Both coordinating solvent and non-coordinating solvents introduce disorder in the material. However, whereas the coordinating solvent substantially influence the Curie temperature, the non-coordinating does not but can lead to e.g. spin-glass behavior at low temperatures.<sup>50</sup> For preparation of  $V(\text{TCNE})_x$ , the precursors are TCNE and bis(benzene)vanadium,<sup>7</sup>  $V(\text{C}_6\text{H}_6)_2$ , or vanadium

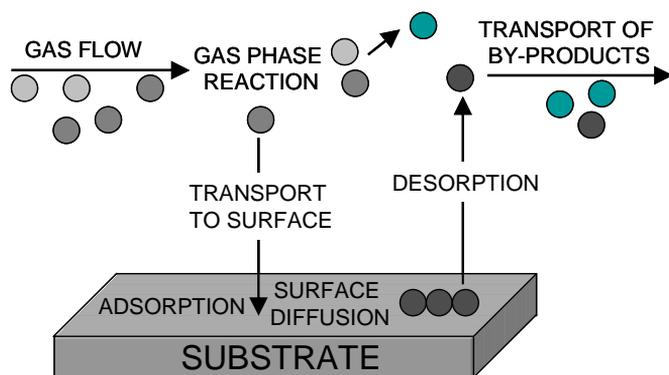
hexacarbonyl,<sup>34</sup>  $V(CO)_6$ . When the reaction has taken place in the organic solvent, the resulting precipitate is filtrated and dried under vacuum, forming an amorphous insoluble magnetic powder.<sup>51</sup> Magnets prepared by this method always contain residual solvent molecules and residual precursors or by-products thereof. As described above, this causes disorder in the material and  $V(TCNE)_x$  prepared by chemical synthesis is extremely air sensitive and decomposes after only a few seconds in air, sometimes in a pyrophoric manner.<sup>7</sup>

### 3.2 Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD)<sup>21, 52, 53</sup> is commonly used in e.g. the semiconductor industry to produce thin films. The precursors are provided in gaseous form and transported (often diluted in a carrier gas) into the chamber where the chemical reaction takes place on or in near vicinity of a substrate. The main drawback of CVD processes is the use of often toxic, corrosive and/or flammable precursors. Frequently, not only the desired material, but also by-products are formed upon the reaction. There are many different types of CVD systems, depending on operating pressures and/or temperatures etc. The low temperature processing of organic materials allow the growth of organic-based magnets on polymer or even paper substrates, enabling production of all-organic devices.<sup>21</sup>

Processing of  $V(TCNE)_x$  by chemical vapor deposition (CVD) was the first step towards applications since the method produces thin films.<sup>54, 55</sup> As these thin films are solvent-free, the detrimental effect of the solvent is eliminated, resulting in enhanced air stability and magnetic properties of the magnets, as compared to the chemically synthesized ones.<sup>55</sup> Apart from  $V(TCNE)_x$ , also  $M(TCNE)_x$ , where  $M = Cr, Nb$  and  $Mo$  have been prepared by the CVD-based technique.<sup>21</sup> Similar to the chemically synthesized magnets, the thin film magnets produced by this CVD-based method contains substantial amounts of oxygen.<sup>55</sup> Therefore has our research group developed an *in situ* ultra-high vacuum (UHV) compatible CVD method,<sup>36, 37</sup> leading to preparation of the first completely oxygen-free  $V(TCNE)_x$  thin films. In this process,  $V(C_6H_6)_2$ , and TCNE are allowed to react in the vacuum chamber and no carrier gas is used to transport the precursors. Hence, this *in situ* preparation allows for usage of more sophisticated surface-sensitive methods for

characterization of e.g. the electronic structure and the magnetic properties of the materials. As mentioned above, by the use of CVD the negative effect of residual solvents is eliminated, but also thin films prepared by this method contain residual precursors and/or by-products from the gas-phase reaction. The UHV compatible CVD method was used for preparation of  $V(\text{TCNE})_x$  in **Paper I** and **Paper II**.



**Figure 3.1** A schematic picture of the steps involved in the CVD process. The figure is based on a model previously presented by e.g. D. de Caro et al.<sup>21</sup>

### 3.3 Physical Vapor Deposition (PVD)

Physical vapor deposition (PVD)<sup>52</sup> is a general term for a group of methods, utilized for thin film deposition. In contrast to CVD, it involves purely physical processes e.g. ion sputtering or resistive heating, rather than chemical reactions. Other differences is that PVD generally is conducted at lower pressures and that no by-products are formed, thus thin film fabrication by PVD is a more “clean” process as compared to the CVD counterpart.

In order to eliminate, not only the material defects induced by residual solvent molecules, but also the defects originating from by-products and/or residual precursors we have developed a PVD-based process for preparation of  $M(\text{organic molecule})_x$  thin films. The principle of this process is that only the materials that should be part of the final thin film, i.e. pure metal and the organic molecules are present in the film preparation. The PVD-based system consists of the PVD source itself, a commercially available Omicron<sup>®</sup> EFM3 UHV e-beam evaporator, and a gas handling system providing the organic molecules. This portable set-up can be

mounted on any (ultra-high) vacuum system, allowing for *in situ* preparation and characterization of the thin film magnets.



**Figure 3.2** Photo of the PVD source, an EFM3 UHV e-beam evaporator from Omicron®.

By depositing the metal by PVD one can avoid the often hazardous and very reactive metal-containing precursor. In addition, high purity metals are commercial available (in contrast to many of the metal-containing precursors), making the method more flexible, but also cheaper, as compared to the UHV compatible CVD process. Hence, by this set-up the metal and/or the organic compound can easily be exchanged. It is also possible to produce organic-based magnets containing more than one metal, or organic compound, as well as of both. This is also possible, however much more complicated, with the two other preparation methods mentioned above. Preparation of  $V(\text{TCNE})_x$  by the PVD-based method produces thin films more resistant towards oxidation but since the outermost surface layer contains  $V^{2+}$  sites  $V(\text{TCNE})_x$  will always be highly reactive (see **Paper III**). Hence, though the material has been developed to a point where it is interesting for device physics research, its commercial potential will depend on how effective the sealing of the devices from atmospheric contaminants can be made. The PVD-based method was used for preparation of  $V(\text{TCNE})_x$  in **Paper III** and **Paper IV** as well as of  $\text{Co}(\text{TCNE})_x$  in **Paper V**. It has also been utilized for fabrication of  $\text{Fe}(\text{TCNE})_x$ <sup>39</sup> and  $\text{Ni}(\text{TCNE})_x$ <sup>30</sup> thin films.

## 4 Experimental Techniques

---

All the research presented in this thesis is based on different types of photoelectron spectroscopy (PES) and near edge X-ray absorption fine structure (NEXAFS) spectroscopy. Those techniques are well suited for studies of the surfaces and interfaces of thin film organic-based magnets. Magnetic characterization of the samples can be performed (among others) by a superconducting quantum interference device (SQUID) magnetometer.

### 4.1 Photoelectron Spectroscopy

Photoelectron spectroscopy (PES) is a very surface sensitive method which can be used for studies of solids, gases or even liquids.<sup>56, 57</sup> The technique is also known as ESCA,<sup>58</sup> electron spectroscopy for chemical analysis. It is based on the photoelectric effect which was discovered by Hertz in 1887 and explained theoretically by Einstein in 1905.<sup>59</sup> The large interest in the method began in the 1960s when high-resolution spectrometers were developed by K. Siegbahn and co-workers in Uppsala, Sweden.<sup>60</sup> Photoelectron spectroscopy is often referred to as a fingerprint technique since each element has its unique PES pattern and all elements except hydrogen can be detected and studied. In addition, many chemical and physical properties of a sample can be obtained by the technique.<sup>56, 59</sup>

#### 4.1.1 The Principle of Photoionization

When a sample is illuminated with photons (e.g. X-rays, UV-light or synchrotron radiation) of known, high enough energy, photoelectrons may be emitted. This is called photoionization or the photoelectric effect.<sup>59</sup> The ejected photoelectrons are collected and detected by a system comprising of electrostatic lenses, an (hemispherical) analyzer, an electron multiplier and a detector. The emitted electrons are analyzed with respect to their kinetic energy,  $E_{kin}$ , and since the

photon energy,  $h\nu$ , is known, the binding energy,  $E_B$ , of the emitted photoelectron can be given from the law of energy conservation. The process may be represented by:<sup>61</sup>

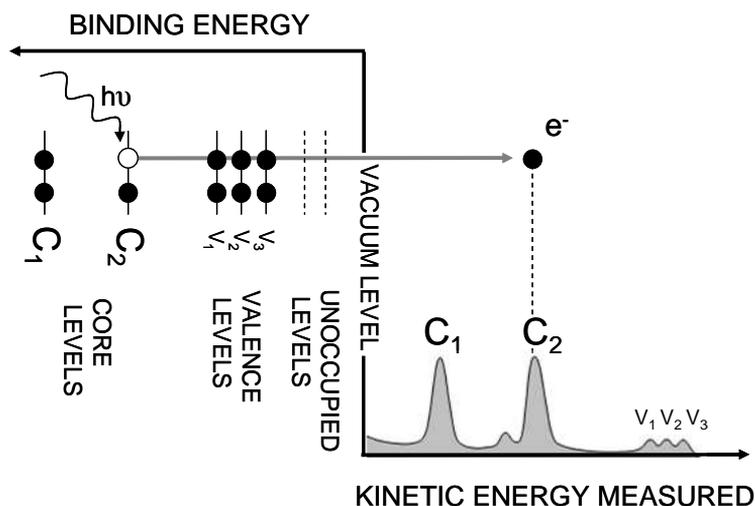
$$E_0 + h\nu = E_+^* + E_{kin} \quad (4.1)$$

where  $E_0$  denotes the ground state, i.e. the total energy of the neutral atom or molecule and  $E_+^*$  accounts for the total energy of the ionized atom or molecule. The binding energy of an electron is as follows:

$$E_B = E_+^* - E_0 \quad (4.2)$$

Hence, by combining equation 4.1 and 4.2 above, the basis of PES is obtained by:

$$E_B = h\nu - E_{kin} \quad (4.3)$$



**Figure 4.1** A schematic figure of a photoelectron spectrum and its correspondence to the ionization of various energy levels. The figure is based on a model previously presented by e.g. W.R. Salaneck et al.<sup>61</sup>

PES is a very surface sensitive method, which is due to the small mean free path (MFP)<sup>62</sup> of the electrons in a sample. The MFP depends on the kinetic energy

of the electrons and determines the depth from which the electrons can escape undisturbed (i.e. without losing energy). The MFP is best illustrated by the so-called universal curve.<sup>62</sup> Electrons emanating from larger distances than the MFP are called secondary electrons and give rise to background in the PES spectra (or remain in the sample), complicating the analysis of a sample.<sup>59</sup>

X-ray photoelectron spectroscopy (XPS), which is used for core level studies, gives a surface sensitivity of approximately 100 Å for electrons of high kinetic energy ( $E_{\text{kin}} > 1000$  eV). The valence levels can be studied by ultra-violet photoelectron spectroscopy (UPS) which is even more surface sensitive with only the first few monolayers ( $\sim 15\text{-}20$  Å) contributing to the signal. In order to be able to detect the electrons escaping from the surface, the MFP of the electrons needs to be longer than the distance between the sample surface and the detector. This requires high vacuum conditions ( $\sim 10^{-6}$  mbar).<sup>63</sup> Besides, to keep the surface free from contaminations during the measurement of a reactive surface, the pressure should be below  $10^{-9}$  mbar, i.e. in the ultra-high vacuum region.<sup>63</sup>

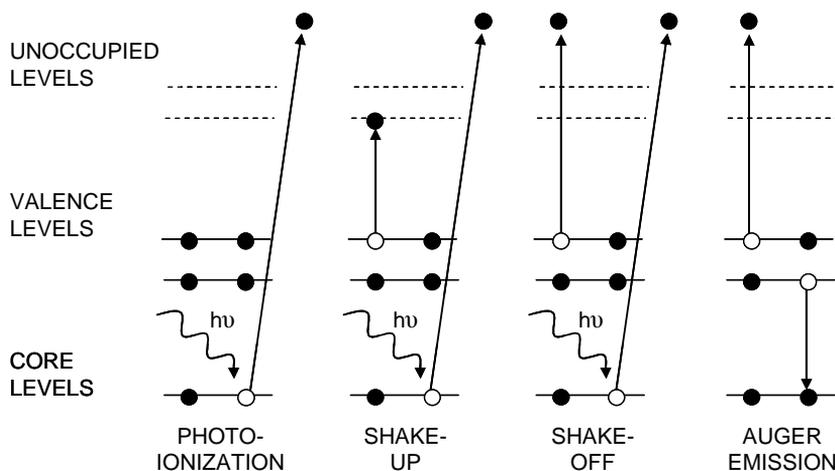
#### **4.1.2 Core Level Spectroscopy (XPS)**

As mentioned above, the core levels are studied by X-ray photoelectron spectroscopy. Since the core electrons of each element have their own unique binding energy this allows for a qualitative analysis of a sample. Furthermore, the PES (of both valence and core levels) technique gives information about the chemical environment, so-called chemical shifts.<sup>64</sup> For example, if a carbon atom is bonded to a more electronegative atom, such as fluorine or oxygen, the more electronegative atom withdraws electronic density from the carbon atom, resulting in that its photoelectron peak is located at higher binding energy than it would have been for a neutral carbon atom. A rough quantitative analysis (error bar 10-20 %) of the relative concentrations of the different elements in a sample can also be performed from a XPS spectrum by using atomic sensitivity factors (ASF),<sup>56</sup> which provide appropriate scaling of the photoelectron peaks. The ASF consider parameters, such as X-ray flux, photoelectric cross-section (excitation probability), MFP of the electrons in the sample, detection efficiency for the electrons emitted from the sample etc.

From the photoelectron peaks the thickness of a thin film onto a substrate can be estimated by the attenuation of the substrate signal after the thin film has been deposited.<sup>63</sup>

$$I = I_0 \exp\left(\frac{-d}{\lambda}\right) \quad (4.4)$$

where  $d$  is the film thickness,  $I_0$  is the original signal,  $I$  is the attenuated signal and  $\lambda$  is the MFP.



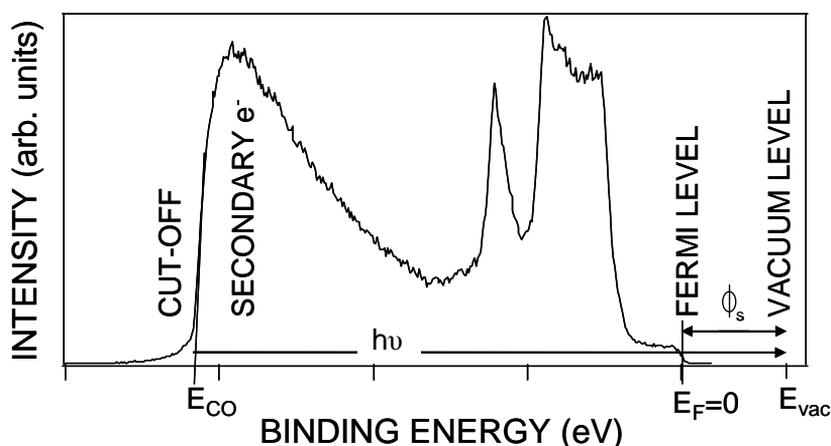
**Figure 4.2** A schematic figure of some possible electron emitting processes, namely photoionization (from a core level), shake-up, shake-off and Auger emission. The figure illustrates well-known concepts previously shown by e.g. W.R. Salaneck et al.<sup>61</sup>

Apart from photoelectron peaks which are the most narrow and intense peaks in a PES spectrum, there may be many other features, resulting from more complex and usually less probable final states. This is due to that the electronic structure of an atom or molecule has time to relax after a photoionization event. Different screening effects give rise to different excited states (each with its own probability). Fig. 4.2 illustrates examples of some possible electron emitting processes, namely photoionization, shake-up, shake-off and Auger emission.<sup>65</sup> Both shake-ups and shake-offs are located at higher binding energies than the photoelectron peak, due to

energy losses. Shake-ups can be used when studying the frontier unoccupied electronic structure (see e.g. **Paper II**).

### 4.1.3 Valence Level Spectroscopy (UPS)

Using ultraviolet light as excitation source was demonstrated in the 1960s,<sup>66</sup> shortly after the development of XPS. The technique, depicted as ultraviolet photoelectron spectroscopy (UPS), is commonly used for studies of the density of occupied electronic states in the valence band. A UPS spectrum also provides information needed for determination of some important parameters of a sample, such as the ionization potential or work function.<sup>61</sup>



**Figure 4.3** A HeI spectrum of gold pointing out some of the information that can be obtained from UPS. See e.g. W.R. Salaneck et al.<sup>61</sup>

The work function,  $\phi_s$ , can be derived from:

$$\phi_s = E_{vac} - E_F = h\nu - E_{CO} \quad (4.5)$$

where  $E_{vac}$  is the vacuum level energy,  $E_F$  is the Fermi level energy,  $h\nu$  is the photon energy and  $E_{CO}$  is the cut-off energy of the secondary electrons.<sup>61</sup>

UPS is a suitable technique for e.g. studies of work function and valence feature changes upon the early stages of doping (for this purpose UPS was used in **Paper I** and **Paper II**, even not shown in the papers).

#### 4.1.4 Reference Level

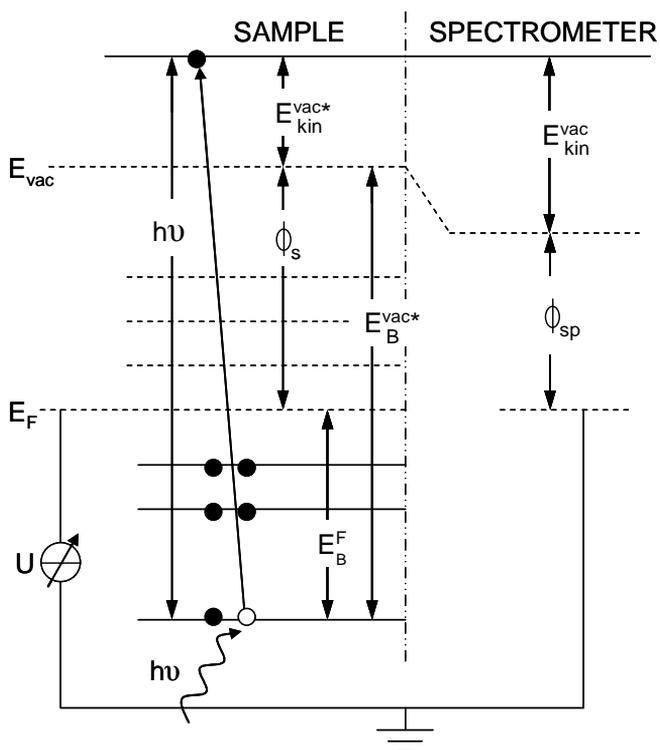
The binding energy scale of a PES spectrum must be defined with respect to a reference. In contrast to gas phase samples where the vacuum level is the natural reference level, the reference level of a solid sample is more complicated. If the sample is in electrical contact with the spectrometer, the Fermi level of the sample and the spectrometer align and the binding energy is measured relative the Fermi level.<sup>63</sup> The photoionization equation for a solid sample can hence be written:<sup>56</sup>

$$h\nu = E_B^F + E_{kin} + \phi_{sp} \quad (4.6)$$

where  $E_B^F$  is the binding energy relative the Fermi energy,  $E_{kin}$  is the kinetic energy of the photoelectrons and  $\phi_{sp}$  is the work function of the spectrometer.

If the sample is poorly conducting the assumption that the sample and spectrometer Fermi level is common is not valid. Positive charges will be accumulated in the sample, leading to that the features in a photoelectron spectroscopy spectrum will appear at higher binding energy than expected. Compensation can be done by an electron flood gun,<sup>63</sup> which ensures electrical neutrality at the surface of the sample.

Sometimes, when work function changes are studied, e.g. upon doping, the vacuum level is used as reference point (see e.g. **Paper II**). If the work function of the sample is known, it enables the adjustment of the binding energy (by adding the work function to the peaks) so that the vacuum level can be used as reference.



**Figure 4.4** Energy level diagram of a sample in electrical contact with the spectrometer. The figure is adopted from Ref [67].

#### 4.1.5 Intensity and Resolution

The intensity of the photoelectron peaks is related to the intensity of the light, MFP of the photoelectrons, photoionization cross-section and elemental concentration. The resolution of a PES spectrum depends on the instrument, e.g. line width of incoming photons (can be reduced by a monochromator) and the resolving power of the analyzer. It depends also on photoionization process, such as the lifetime of the ionized state. Surface roughness and sample charging can also affect the widths of the peaks.<sup>59</sup>

## 4.2 Photon Sources

Photon sources can be either fixed or tunable.<sup>59</sup> Fixed sources are e.g. the X-ray gun and the helium discharge lamp, while tunable light is produced at a synchrotron facility. In the X-ray gun thermally emitted electrons are accelerated towards an anode. When the electrons hit the anode, they create holes in the core

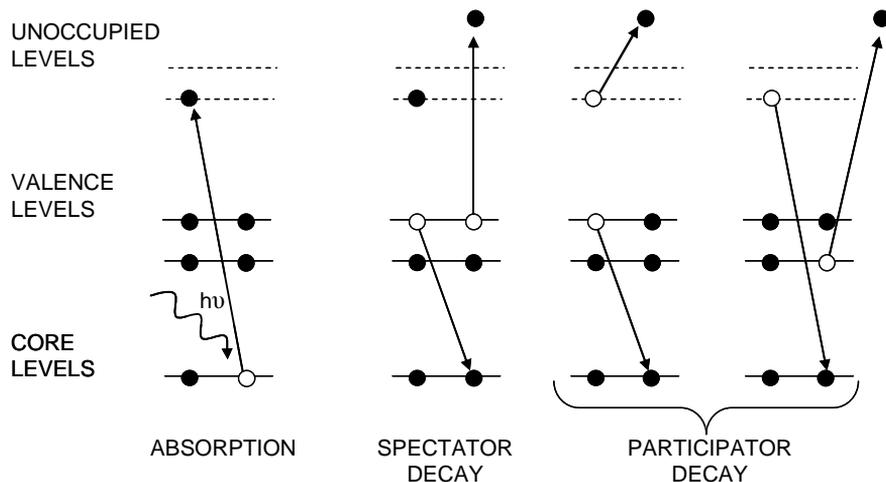
shells of the anode material, resulting in de-excitations from higher energy levels and hence emission of X-ray radiation. The most commonly used anodes are aluminum or magnesium, producing X-rays of  $\text{AlK}_\alpha = 1486.6$  eV and  $\text{MgK}_\alpha = 1253.6$  eV, respectively. A helium discharge lamp contains helium gas kept in an enclosure and when applying an electric field the gas becomes ionized. Upon relaxation of the ionized (excited) atoms in the gas, photons of  $\text{HeI} = 21.2$  eV or  $\text{HeII} = 40.8$  eV are emitted.<sup>59</sup>

Synchrotron radiation is produced by circulating charged particles, usually electrons, in an ultra high vacuum storage ring at relativistic speeds, i.e. close to that of light. When the charges are accelerated by bending magnets or insertion devices, such as wigglers or undulators,<sup>68</sup> they emit electromagnetic radiation. The energy of the synchrotron light typically covers a large range of the energy spectrum, ranging from infrared (IR) to hard X-rays and by using a monochromator the energy of the light can be tuned to suit a specific experiment, such as PES or absorption spectroscopy (discussed below). Other characteristics of synchrotron radiation include high photon flux, brilliance (or brightness) and polarized light.<sup>69</sup> Several beamlines are attached to the storage ring and each of them is dedicated to one or a few specific techniques. The development of synchrotron radiation started in the 1940s and today there are about 40 facilities in the world of which one, MAX-lab<sup>70</sup> (where the experiments in this thesis were performed) is located in Lund, Sweden.<sup>69</sup>

### 4.3 Absorption Spectroscopy

Near edge X-ray absorption fine structure (NEXAFS) spectroscopy is a method for studying the frontier unoccupied electronic states in presence of a core hole.<sup>71</sup> The region studied by NEXAFS is the actual absorption edge (onset) and about 30 eV above it. There are two different ways of performing the measurements, i.e. transmission or photoyield mode. In the transmission mode the X-rays that are transmitted through the sample are measured. This mode has limited use since it requires thick and free-standing films. The photoyield mode measures the absorption in a more indirect way, by studying the decay products. The decay products relates to emitted electrons (electron yield) or fluorescent photons (fluorescent yield) which are produced when an excited atom relax. The electron yield is most suitable for

light elements and therefore it appears as the best alternative for studies of organic materials. In the electron yield, absorption of photons is followed by excitation of core electrons to originally (bound) unoccupied states. Those states decay and therefore an absorption event is followed by a dramatic increase of the number emitted electrons. The absorption and the possible decay channels are illustrated in Fig. 4.5.



**Figure 4.5** Principle of absorption and the following Auger processes (decay channels). See e.g. N. Mårtensson et al.<sup>72</sup>

Furthermore, the electron yield can be performed in two different ways, namely total yield and partial yield.<sup>71</sup> In total yield are all electrons counted, both Auger electrons and photoelectrons. In partial yield only the Auger electrons are counted, leading to a more surface sensitive analysis than the total electron yield mode. Since the energy must be swept across the onset energy, NEXAFS implies the use of a tunable photon source. As core levels are involved in the process, NEXAFS is an elemental specific technique and can provide information regarding both the elemental composition as well as the local chemical environment. For example, the technique can be a useful tool for determining the nature of the frontier unoccupied electronic structure (see e.g. **Paper I**, **Paper II**). NEXAFS can also be used for studying the orientation of

the molecules by measuring the sample at different rotations (relative to the analyzer).<sup>71</sup>

#### 4.4 Resonant Photoelectron Spectroscopy (RPES)

Similar to absorption spectroscopy the decay products after an absorption event are studied in resonant photoelectron spectroscopy (RPES).<sup>72</sup> However, in RPES it is the binding energy of the decay products versus the electron yield that are considered. The experiment is performed by sweeping the photon energy in discrete steps over a specific absorption edge while monitoring the electrons emitted from the valence region. The lifetime of a core-excited state is on the femtosecond scale and when it decays it can do so in different ways as shown in Fig. 4.5. For the non-radiative emission there are two Auger decay channels, participator and spectator decay, respectively, and for RPES the participator decay is of main interest. The participator and spectator decays can be distinguished by their energy dispersions, for participator decay the peaks appear at constant binding energy while the binding energy of spectator decay depends linearly on the photon energy. In participator decay the final states are energetically the same as for the valence PES, i.e. one valence hole, however the transition matrix elements are different, namely dipole for PES and Coulomb for RPES. For the spectator decay the final state is more complex with two holes and one electron.<sup>72</sup>

Since core excitations are site-specific, RPES allows for determination of the origin of certain valence features and e.g. the origin of the HOMO of a compound (see e.g. **Paper V**). RPES can also be used for charge transfer dynamics studies,<sup>72</sup> mainly for small systems since a detailed interpretation of RPES spectra requires complex theoretical calculations.

#### 4.5 Superconducting Quantum Interference Device (SQUID)

A superconducting quantum interference device (SQUID) magnetometer is based on the Josephson effect of superconductors and can detect extremely weak magnetic fields (even those produced by brain activity).<sup>73</sup> The Josephson effect occurs when current flows across two superconducting materials which are separated by a thin isolating layer.<sup>73</sup> This set-up is known as a Josephson junction. A SQUID consists of a superconducting ring containing two Josephson junctions

and the Josephson effect appears when a sample is passed through the ring. The induced current is proportional to the magnetization of the sample.<sup>74, 75</sup> A SQUID measures the quantitative magnetization and the data can be used to e.g. determine the Curie temperature or the magnetic moment of atoms in a sample. The magnetization is measured either as a function of temperature in a constant magnetic field or as a function of applied magnetic field at constant temperature. The SQUID method was used by our collaborators in Uppsala for obtaining some of the data in **Paper III**.



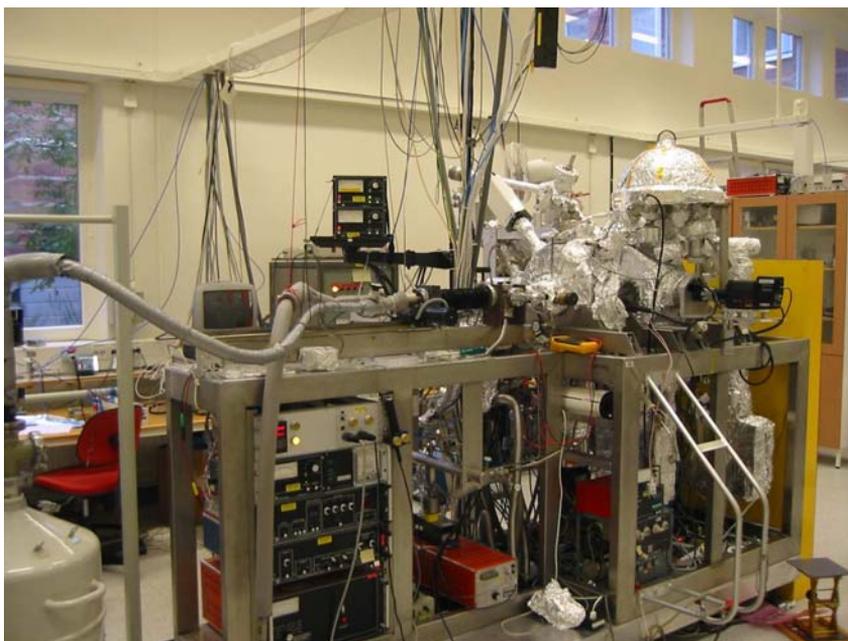
## 5 Equipment

---

The work presented in this thesis has been performed at the two photoelectron spectrometers “Scienta” and “Moses” in the laboratories of Surface Physics and Chemistry Division at Linköping University. Additional measurements that required a tunable photon source were performed at beamline I311 and D1011 at the Swedish national synchrotron laboratory, MAX-lab<sup>70</sup> in Lund, Sweden.

### 5.1 Moses

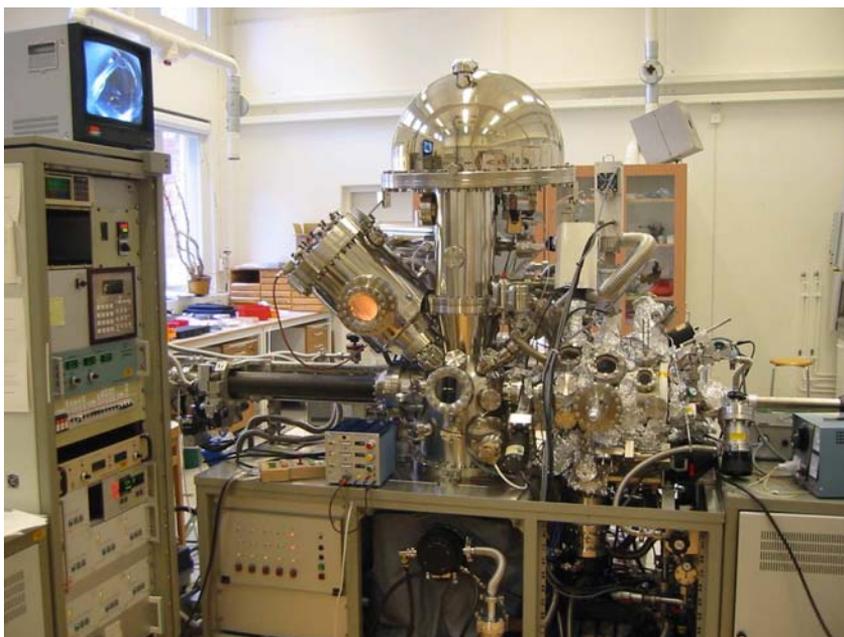
Moses is a custom-built photoelectron spectrometer for X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS). The system consists of a hemispherical analyzer and an electron detector. It has three vacuum chambers namely, introduction, preparation and analysis chamber. The analysis chamber is equipped with a non-monochromatized X-ray source ( $h\nu$ :  $AlK_{\alpha} = 1486.6$  eV) and a monochromatized helium discharge lamp ( $h\nu$ : HeI = 21.2 eV and HeII = 40.8 eV). The preparation chamber allows for *in situ* sample preparation and is equipped with an ion sputter gun, a gas handling system (for sample preparation from gas- or vapor phase) and possibilities to mount deposition sources. The sample temperature can be controlled in the range -190 °C by liquid nitrogen, up to 300 °C by resistive heating. The base pressure is better than  $1 \cdot 10^{-9}$  mbar and obtained by a combination of turbo molecular, ion getter and cryogenic pumps. Parts of the work presented in **Paper I** and **Paper II** were performed in Moses.



*Figure 5.1 The custom-built photoelectron spectrometer “Moses”.*

## 5.2 Scienta

The commercially available Scienta<sup>®</sup> ESCA 200 spectrometer is equipped with a hemispherical analyzer combined with a multi-channel plate electron detector system. Similar to the custom-built spectrometer, the vacuum system comprises of three chambers, introduction, preparation and analysis, respectively. Two photon sources are available, a monochromatized X-ray source ( $h\nu$ :  $\text{AlK}_\alpha = 1486.6 \text{ eV}$ ) and a helium discharge lamp providing non-monochromatized helium light ( $h\nu$ :  $\text{HeI} = 21.2 \text{ eV}$  and  $\text{HeII} = 40.8 \text{ eV}$ ). The preparation chamber has an ion sputter gun for preparation of ultra-clean surfaces, free ports where deposition sources, such as the Omicron<sup>®</sup> EFM3 UHV e-beam evaporator can be mounted, allowing for sample preparation *in situ*. A gas handling system is also available, enabling deposition of molecules from gas or vapor phase. The temperature of the samples can be controlled in the region  $-190 \text{ }^\circ\text{C}$  to  $300 \text{ }^\circ\text{C}$ . The system is pumped by turbo molecular, ion getter and titanium sublimation pumps, leading to a base pressure in the low  $10^{-10}$  mbar region in both the preparation and the analysis chamber. The photoelectron spectroscopy results in **Paper III** and parts of the results in **Paper IV** and **Paper V** were obtained at Scienta.



*Figure 5.2* The Scienta<sup>®</sup> ESCA 200 photoelectron spectrometer.

### 5.3 Beamline I311

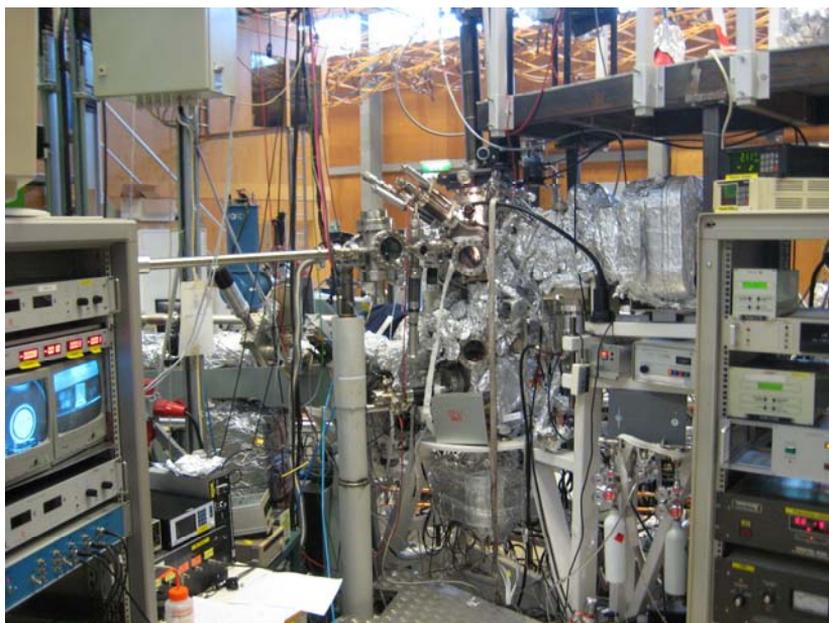
The undulator-based beamline I311<sup>76</sup> is located at the third generation 1.56 GeV storage ring MAX II at the Swedish national laboratory, MAX-lab, in Lund. The photon energy is in the range 30 to approximately 1500 eV and is monochromatized by a plane grating monochromator. The beamline has two end-stations and the first is used for high resolution photoelectron spectroscopy (PES) and near edge X-ray absorption fine structure (NEXAFS). This end station is equipped with a Scienta<sup>®</sup> ESCA 200 hemispherical electron energy analyzer and the base pressure in the preparation and analysis chambers is  $1 \cdot 10^{-9}$  mbar. *In situ* sample preparation can be performed by mounting deposition sources on the preparation and analysis chambers. The NEXAFS spectra shown in **Paper I** and **Paper II** were recorded at I311.



*Figure 5.3* Beamline I311 at MAX-lab.

#### 5.4 Beamline D1011

Beamline D1011<sup>77</sup> is based on bending magnets and is just like I311 located at MAX II in MAX-lab. It provides photon energy in the region between 30 to 1500 eV. The main feature of this beamline is the possibility to use circularly polarized light by tilting the e-beam in MAX-II allowing performance of X-ray magnetic circularly dichroism (XMCD) measurements. The beamline has two experimental stations, back-end and front-end, respectively. The front-end chamber, which was used for the experiments for this thesis, has a preparation and an analysis chamber, enabling *in situ* sample preparation. It is equipped with a Scienta ESCA 200 hemispherical electron energy analyzer for PES and a purpose built multichannel plate (MCP) detector for absorption spectroscopy measurements. The pressure of the system is low  $10^{-10}$  mbar. The NEXAFS spectra shown in **Paper IV** as well as PES, NEXAFS and resonant photoelectron spectroscopy (RPES) results shown in **Paper V** were obtained at D1011.



*Figure 5.4 The front-end station at beamline I1011 at MAX-lab.*



## 6 Summary and Future Outlook

---

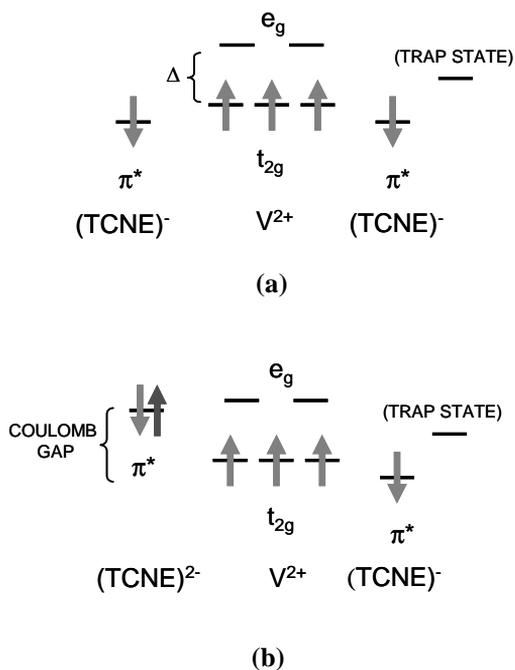
In this last chapter a review of the work presented in the thesis is provided. The two last paragraphs also contain a short discussion about our current work and a future outlook.

### 6.1 Background

As the organic-based magnet vanadium tetracyanoethylene,  $V(\text{TCNE})_x$ , is an attractive material for spintronics devices, knowledge about its electronic and chemical structure as well as its interface with ferromagnetic (FM) metals are of high importance. Surface studies by different photoelectron and absorption spectroscopy techniques are well suited for this purpose and were therefore utilized for the work presented in the thesis. However, the material was first prepared as powder<sup>7</sup> and later as *ex situ* prepared thin films,<sup>54, 55</sup> of which both are extremely air sensitive. Therefore these very surface-sensitive measurement techniques were not feasible and hence the electronic structure of the material remained unknown for long time. In our research group the work about organic-based magnets started with experimental and theoretical studies of a model compound of  $V(\text{TCNE})_x$ , namely Rb-doped TCNE,<sup>38</sup> which provided information about the nature of the charge carriers and some insight into the magnetic properties of  $V(\text{TCNE})_x$ . The next step was development of a new *in situ* preparation method of  $V(\text{TCNE})_x$  by an ultra-high vacuum (UHV) compatible process based on chemical vapor deposition (CVD), resulting in completely oxygen-free thin films.<sup>36</sup> This *in situ* method enabled for the first time measurements by sophisticated surface analysis methods such as photoelectron spectroscopy and absorption spectroscopy.

## 6.2 Summary of the Thesis

To be able to correct understand the (spin-polarized) injection and transport properties of  $V(\text{TCNE})_x$ , the accepting and transporting levels of electrons and holes of the material must be known. A model of the electronic structure of  $V(\text{TCNE})_x$  was suggested by Prigodin *et al*, but without being confirmed experimentally.<sup>33</sup> In this model, both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the material was proposed to be TCNE-derived. The model was later modified by experimental resonant photoelectron spectroscopy (RPES) results of the frontier *occupied* electronic structure performed by our research group<sup>36</sup> since it was shown that the HOMO of  $V(\text{TCNE})_x$  is actually mainly derived from  $V(3d)$  and not only from TCNE. However, no experimental results of the frontier *unoccupied* electronic structure existed at this time. Therefore, the purpose of **Paper I** was to gain information about the frontier unoccupied electronic structure of  $V(\text{TCNE})_x$ . With this intention,  $V(\text{TCNE})_x$ , Na-doped TCNE and pristine TCNE were studied by X-ray and UV photoelectron spectroscopy (XPS and UPS) as well as with near edge X-ray absorption fine structure (NEXAFS) spectroscopy. Na-doped TCNE can act as model system of  $V(\text{TCNE})_x$  since Na n-dopes TCNE but has the advantage that it is less complex than  $V(\text{TCNE})_x$ . The spectra of the two compounds are quite similar with the main exception that the  $V(\text{TCNE})_x$  peaks are slightly broader which can be attributed to structural disorder of  $V(\text{TCNE})_x$ . The experimental results were interpreted together with theoretical calculations of the NEXAFS spectra of pristine TCNE as well as of Na-doped TCNE. The calculations were performed by our collaborators at KTH in Stockholm. By comparing the experimental and theoretical results of pristine TCNE, the contributions from the various carbon species (cyano and vinyl) could be disentangled. In contrast to the occupied electronic structure,<sup>36, 37</sup> which is strongly hybridized, this study showed that there is no (or very little) hybridization between vanadium and TCNE in the unoccupied frontier electronic structure, which means that the LUMO is either localized on vanadium *or* on TCNE.

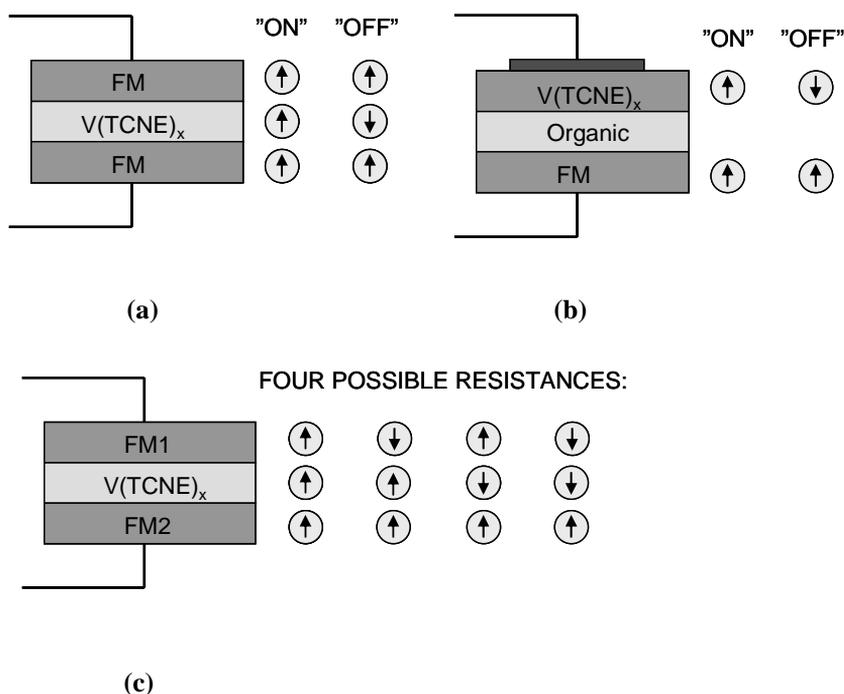


**Figure 6.1** Simplified picture of the electronic structure of  $V(\text{TCNE})_x$ . (a) Ground state. (b) With one extra electron added. The figure is adopted from **Paper II** (copyright © Elsevier B.V.).

In **Paper II**, the study started in **Paper I** in was continued, resulting in determination of the LUMO location and hence a more complete picture of the frontier electronic structure of  $V(\text{TCNE})_x$ . XPS and NEXAFS of  $V(\text{TCNE})_x$  and of Na-doped  $V(\text{TCNE})_x$  were performed in order to obtain the results. The LUMO was determined to mainly be derived from the  $\text{TCNE}^-$  states by studying the shake-ups of the XPS spectra and the NEXAFS spectra upon step-wise Na-doping. In addition, it was shown that there are trap states for electron transport present in the material, most likely originating from benzene-related residual precursors and/or other by-products from the CVD-based preparation process. It is important to note that the trap states are located at lower energy than the  $\text{TCNE}^{2-}$  states which means that they will be occupied by injected electrons to the material *before* the  $\text{TCNE}^-$  states. Hence, the trap states likely leads to increased energetic disorder and decreased

mobility of the material. The results obtained from **Paper I** and **Paper II** have strong implication on the design of devices based on  $V(TCNE)_x$ , as the frontier electronic structure is highly important for its charge transport and magnetic properties.

As shown by **Paper II**, (benzene-related) impurities induce disorder in the material and can work as trap states for electron transport. The impurities may also function as oxygen-reaction sites. Hence, it would be desirable (or even necessary) to develop organic-based magnets without this type of impurities. In **Paper III** a new preparation method, based on physical vapor deposition (PVD), of hybrid organic-based magnets is presented. The principle of this method is that no other materials than the ones that should be part of the final films is present in the preparation process, i.e. only pure vanadium and TCNE in the case of  $V(TCNE)_x$  preparation. This would lead to a less disordered material since it lacks contamination from residual precursors and/or by-products thereof. Just like the CVD process reported by our group the thin films of  $V(TCNE)_x$  prepared by the PVD-based process is prepared under UHV conditions and are completely free from oxygen. The thin films of  $V(TCNE)_x$  were studied by XPS, UPS and compared with results of  $V(TCNE)_x$  prepared by CVD. The magnetic characterization was performed with a superconducting quantum interference device (SQUID) by collaborators in Uppsala. The first study of  $V(TCNE)_x$  prepared by this technique showed that those films are more resistant towards oxygen as compared to previously reported CVD-prepared thin films. However, it is important to note that the outermost surface of  $V(TCNE)_x$  always will be highly reactive due to the  $V^{2+}$  sites present. The first result on the critical temperature of  $V(TCNE)_x$  prepared by this method is in very well agreement ( $T_C \sim 365$  K) with previously shown values of  $V(TCNE)_x$ , both for thin films and powders.<sup>7, 34</sup> Furthermore, the method is much more flexible since pure metal is used instead of the often hazardous and not always commercially available precursors. This method also easily enables preparation of other members of the  $M(TCNE)_x$  family as well as  $M'M''(TCNE)_x$  (with two or even up to three metals), see **Paper III**. So far this preparation method has been used for preparation of  $Fe(TCNE)_x$ ,<sup>39</sup>  $Ni(TCNE)_x$ <sup>30</sup> and  $Co(TCNE)_x$  (see **Paper V**).



**Figure 6.2** The spin valve structures based on  $V(TCNE)_x$ . (a) With two identical FM contacts. (b) With  $V(TCNE)_x$  as soft magnet.<sup>48</sup> (c) With two different FM contacts. The figure is adopted from **Paper IV** (copyright © Elsevier B.V.).

Since the goal is to fabricate spintronic devices based on  $V(TCNE)_x$ , the interface between FM metals and  $V(TCNE)_x$  has strong implication of both the spin injection and detection properties. In **Paper IV** the interfaces of Ni/ $V(TCNE)_x$  as well as of a model system, Ni/TCNE, were studied with PES and NEXAFS. The results show that Ni interacts with both the cyano and the vinyl groups of TCNE in  $V(TCNE)_x$ . As chemical interaction affects both spin injection and detection negatively by modifying the LUMO, likely destroying the magnetic network at the surface, the results hence indicate that there is need for a buffer layer between Ni and  $V(TCNE)_x$ . Most likely this could be extended to be valid for  $V(TCNE)_x$  and any FM contact. In the same paper two new spin valve designs based on  $V(TCNE)_x$  were proposed. The basis of these new device designs is to use  $V(TCNE)_x$  as spin-transporting and spin-filtering layer sandwiched *in between* the two ferromagnetic

contacts, i.e. FM1/V(TCNE)<sub>x</sub>/FM2, instead of using V(TCNE)<sub>x</sub> as the soft magnetic contact.<sup>48</sup> These devices would make use of the fully spin-polarized transport levels of V(TCNE)<sub>x</sub> and hence it would both enhance and preserve the spin polarizations that are injected from the FM contacts. Two identical FM contacts could be used, which is an advantage in the fabrication process point of view, or it could be built with two different FM contacts. The former device would give the standard spin valve on/off functionality, whereas the latter would enable four different resistances to be obtained. To the best of our knowledge no device based on V(TCNE)<sub>x</sub> has been realized so far, and remains a goal of our research.

As vanadium ions always are highly reactive towards e.g. oxygen, it would be desirable to exchange vanadium in V(TCNE)<sub>x</sub> with another metal. The prerequisite for such metal would be that it results in a magnet which is air stable, semiconducting and magnetically ordered at room temperature. With the aim to understand the key design criteria for developing organic-based magnets with magnetic ordering above room temperature we have started to study M(TCNE)<sub>x</sub> materials with significantly lower critical temperatures than room temperature and compared them with V(TCNE)<sub>x</sub>. In **Paper V** we present the first results on the electronic structure of Co(TCNE)<sub>x</sub>, ( $T_C \sim 44 \text{ K}^{13}$ ) performed by XPS, NEXAFS and resonant photoelectron spectroscopy (RPES). The XPS data suggests that Co(TCNE)<sub>x</sub> contains local bonding disorder, unlike V(TCNE)<sub>x</sub> which can be grown virtually defect free. The HOMO was determined by RPES to mainly be derived from TCNE<sup>-</sup> units while the Co(3d) states are localized at higher binding energies. This is in sharp contrast to the case for V(TCNE)<sub>x</sub> where V(3d) is mainly responsible for the HOMO.<sup>36</sup> However, it resembles the results of the electronic structure that we have obtained previously for Fe(TCNE)<sub>x</sub> ( $T_C \sim 122 \text{ K}^{13}$ ) for which the HOMO also is TCNE<sup>-</sup>-derived.<sup>39</sup> Nevertheless, it was not possible to perform calculations due to the lack of fine structure in the Co(TCNE)<sub>x</sub> Co L-edge NEXAFS spectra. This could be done for both the Fe L-edge of Fe(TCNE)<sub>x</sub><sup>39</sup> and of the V L-edge of V(TCNE)<sub>x</sub>,<sup>36</sup> indicating that the crystal field in Co(TCNE)<sub>x</sub> is much weaker than that of Fe(TCNE)<sub>x</sub> and especially weaker than the crystal field of V(TCNE)<sub>x</sub>. However, the similarities in the electronic structure between Co(TCNE)<sub>x</sub> and Fe(TCNE)<sub>x</sub> are in line with the significantly lower critical temperature as compared

to  $V(\text{TCNE})_x$  but if the reason for the lower critical temperature is due to the disorder in the material, the very weak crystal field, or a combination of both is however difficult to say.

### 6.3 Current Studies

Since  $V(\text{TCNE})_x$  reacts with FM metals (see **Paper IV**) this indicates the need for a buffer layer between the two materials and we are currently focusing on finding a proper material for this purpose. However, due to the very reactive nature of  $V(\text{TCNE})_x$  this has shown to be an intricate task. For example LiF, which has been frequently used as buffer layer in organic electronics,<sup>78</sup> was deposited on top of  $V(\text{TCNE})_x$ , but the results indicate that the fluorine reacts with the vanadium ions. The most promising buffer layer so far seems to be alkyl chains ( $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_3$ ) since the first results indicate no reaction between alkyl groups and vanadium or TCNE. The use of long alkyl chains as buffer layers in organic electronics has previously been demonstrated by other groups.<sup>79, 80</sup>

### 6.4 Future Outlook

It is difficult to predict the timescale before any product based on organic-based magnets may reach the market. With properties such as low weight, potentially cheaper production, biocompatibility, light-induced magnetism, solubility in organic solvents etc.,<sup>2</sup> they for sure have potential to be used in future electronic products. One can draw parallels between the development of organic-based magnets and organic electronics, conducting polymers were discovered in 1977,<sup>81</sup> the first prototype device was demonstrated in 1990<sup>82</sup> and the first product entered the market about 20 years after the first discovery (organic light emitting diode (OLED) displays, by Tohoku Pioneer in 1999). Initially, conducting polymers were thought of as replacement of metallic conductors.<sup>83</sup> After a few years it was realized that they are unable to compete with copper but they found a new application area in LEDs. Today, mainly molecules, not polymers, are used. The first room temperature organic-based magnet,  $V(\text{TCNE})_x$ , was discovered in 1991 as a powder magnet and 10 years later the first thin films of the compound were reported. Preparation as thin films was the first step towards applications and if organic-based magnets follow the same timescale as organic electronics this would

mean that products could be on the market in approximately ten to twenty years from now. However, due to the oxygen sensitivity of  $V(\text{TCNE})_x$ , its commercial potential will depend on the effectiveness of sealing the device from atmospheric contamination, nevertheless, it is an interesting material for pursuing research on device physics, e.g. fabrication of spin valves. Similar to the case of organic electronics, organic-based magnets are unlikely to compete with their metallic counterparts. However, they have shown properties not seen in metallic magnets and will most likely find their own application areas, e.g. in spintronics. It is worth to note that they have also been suggested for other applications, such as functional coatings on e.g. plastic or paper for microwave absorption and magnetic shielding.<sup>10</sup>

Before prototype devices based on organic-based magnets, in particular  $V(\text{TCNE})_x$ , can be reality there are a number of issues that should be addressed. First of all, it is important to find a suitable buffer layer to sandwich in between  $V(\text{TCNE})_x$  and FM metals (as described in the paragraph above). Furthermore, it is adequate, or even necessary, to increase the thin film growing speeds of the current CVD- and PVD-based processes. This would save a lot of time when starting the first attempts to fabricate devices based on  $V(\text{TCNE})_x$ .

Most likely, the first commercial applications will rely on a less air sensitive magnets than  $V(\text{TCNE})_x$ . Therefore, the search for other room temperature magnetically ordered semiconducting materials which are less air sensitive than  $V(\text{TCNE})_x$  should also be continued.

# References

---

- <sup>1</sup> M. Fahlman and W.R. Salaneck, Surfaces and interfaces in polymer-based electronics, *Surf. Sci.* **500**, 904 (2002).
- <sup>2</sup> J. Miller and A.J. Epstein, Molecule-Based Magnets- An Overview, *MRS Bullet.* **25**, 21 (2000).
- <sup>3</sup> J. Veciana and H. Iwamura, Organic Magnets, *MRS Bullet.* **25**, 41 (2000).
- <sup>4</sup> A.J. Epstein, Organic-Based Magnets: Opportunities in Photoinduced Magnetism, Spintronics, Fractal Magnetism and Beyond, *MRS Bullet.* **28**, 492 (2003).
- <sup>5</sup> D.A. Pejakovic, C. Kitamura, J.S. Miller, and A.J. Epstein, Photoinduced Magnetization in the Organic-Based Magnet  $\text{Mn}(\text{TCNE})_x \cdot y(\text{CH}_2\text{Cl}_2)$ , *Phys. Rev. Lett.* **88**, 057202 (2002).
- <sup>6</sup> J.S. Miller, Organic Magnets - A History, *Adv. Mater.* **14**, 1105 (2002).
- <sup>7</sup> J.M. Manriquez, G.T. Yee, R.S. McLean, A.J. Epstein, and J.S. Miller, A room-temperature molecular/organic-based magnet, *Science* **252**, 1415 (1991).
- <sup>8</sup> P-M. Allemand, K.C. Khemani, A.F. Wudl, K. Holczer, S. Donovan, G. Grüner, and J.D. Thompson, Organic molecular soft ferromagnetism in a fullerene  $\text{C}_{60}$ , *Science* **253**, 301 (1991).
- <sup>9</sup> M. Takahashi, P. Turek, Y. Nakazawa, M. Tamura, K. Nozawa, D. Shiomi, M. Ishikawa, and M. Kinoshita, Discovery of a quasi-1D organic ferromagnet, p-NPNN, *Phys. Rev. Lett.* **67**, 746 (1991).
- <sup>10</sup> A.J. Epstein and B.G. Morin, Molecular-based magnets comprising vanadium tetracyanoethylene complexes for shielding electromagnetic fields, US patent 5821453, 1998.
- <sup>11</sup> W.J.M. Naber, S. Faez, and W.G. van der Wiel, Organic spintronics, *J. Phys. D: Appl. Phys.* **40**, R205 (2007).

## References

---

- <sup>12</sup> M.A. Gîrțu, C.M. Wynn, J. Zhang, J.S. Miller, and A.J. Epstein, Magnetic properties and critical behavior of  $\text{Fe}(\text{tetracyanoethylene})_2 \cdot x(\text{CH}_2\text{Cl}_2)$ : A high- $T_c$  molecule-based magnet, *Phys. Rev. B* **61**, 492 (2000).
- <sup>13</sup> J. Zhang, J. Ensling, V. Ksenofontov, P. Gütlich, A.J. Epstein, and J.S. Miller,  $[\text{M}^{\text{II}}(\text{tcne})_2] \cdot x\text{CH}_2\text{Cl}_2$  (M = Mn, Fe, Co, Ni) Molecule-Based Magnets with  $T_c$  Values above 100 K and Coercive Fields up to 6500 Oe, *Angew. Chem. Int. Ed.* **37**, 657 (1998).
- <sup>14</sup> C.M. Wynn, M.A. Gîrțu, J. Zhang, J.S. Miller, and A.J. Epstein, Reentrance in the  $\text{Mn}(\text{tetracyanoethylene})_x \cdot y(\text{CH}_2\text{Cl}_2)$  high- $T_c$  molecule-based ferrimagnet, *Phys. Rev. B* **58**, 8508 (1998).
- <sup>15</sup> S. Blundell, *Magnetism in Condensed Matter* (Oxford University Press, New York, 2001).
- <sup>16</sup> H. Benson, *University Physics*, (Wiley, New York, 1996).
- <sup>17</sup> C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, 1996).
- <sup>18</sup> M.A. Gîrțu and M. Fahlman, *Hybrid Organic-Inorganic Nanostructured Magnets*, in manuscript.
- <sup>19</sup> J-W. Yoo, R.S. Edelstein, D.M. Lincoln, N.P. Raju, and A.J. Epstein, Photoinduced Magnetism and Random Magnetic Anisotropy in Organic-Based Magnetic Semiconductor  $\text{V}(\text{TCNE})_x$  Films, for  $x \sim 2$ , *Phys. Rev. Lett.* **99**, 157205 (2007).
- <sup>20</sup> E.B. Vickers, T.D. Selby, and J.S. Miller,  $\text{Ni}[\text{TCNE}]_2 \cdot z\text{CH}_2\text{Cl}_2$  ( $T_c = 13$  K) and  $\text{V}_x\text{Ni}_{1-x}[\text{TCNE}]_y \cdot z\text{CH}_2\text{Cl}_2$  solid solution room temperature magnets, *J. Am. Chem. Soc.* **126**, 3716 (2004).
- <sup>21</sup> D. de Caro, C. Faulmann, and L. Valade, Ligand Influence on Connectivity and Processing: Magnetic Crystals Based on Metalloceniums and Films of TCNE-Based Magnets (TCNE = Tetracyanoethylene) *Chem. Eur. J.* **13**, 1650 (2007).
- <sup>22</sup> B.B. Kaul, M.A. Taylor, M.J. Whitton, and G.T. Yee, Beyond TCNE: new building blocks for molecule-based magnets, *Synth. Met.* **122**, 471 (2001).
- <sup>23</sup> E.B. Vickers, T.D. Selby, and J.S. Miller, Magnetically Ordered ( $T_c = 200$  K) Bis(tetracyanopyrazine)vanadium,  $\text{V}[\text{TCNP}]_2 \cdot y\text{CH}_2\text{Cl}_2$ , *J. Am. Chem. Soc.* **126**, 3716 (2003).

- 24 J.P. Fitzgerald, B.B. Kaul, and G.T. Yee, Vanadium[dicyanoperfluorostilbene]<sub>2</sub>·yTHF: a molecule-based magnet with  $T_C \approx 205$  K, *Chem. Commun.* **1**, 49 (1999).
- 25 K.I. Pokhodnya, V. Burtman, A.J. Epstein, J.W. Raebiger, and J.S. Miller, Control of Coercivity in Organic-Based Solid Solution  $V_xCo_{1-x}[TCNE]_2 \cdot zCH_2Cl_2$  Room Temperature Magnets, *Adv. Mater.* **15**, 1211 (2003).
- 26 E.B. Vickers, A. Senesi, and J.S. Miller, Ni[TCNE]<sub>2</sub>·zCH<sub>2</sub>Cl<sub>2</sub> ( $T_C = 13$  K) and  $V_xNi_{1-x}[TCNE]_y \cdot zCH_2Cl_2$  solid solution room temperature magnets, *Inorg. Chim. Acta* **357**, 3889 (2004).
- 27 K.I. Pokhodnya, E.B. Vickers, M. Bonner, A.J. Epstein, and J.S. Miller, Solid solution  $V_xFe_{1-x}[TCNE]_2 \cdot zCH_2Cl_2$  room-temperature magnets, *Chem. Mater.* **16**, 3218 (2004).
- 28 R. Jain, K. Kabir, J.B. Gilroy, K.A.R. Mitchell, K-C. Wong, and R.G. Hicks, High-temperature metal-organic magnets, *Nature* **445**, 291 (2007).
- 29 J.S. Miller and K.I. Pokhodnya, Formation of Ni[C<sub>4</sub>(CN)<sub>8</sub>] from the reaction of Ni(COD)<sub>2</sub>(COD=1,5-cyclooctadiene) with TCNE in THF, *J. Mater. Chem.* **17**, 3585 (2007).
- 30 P. Bhatt, A. Kancierzewska, E. Carlegrim, M. Kapilashrami, L. Belova, K.V. Rao, and M. Fahlman, Ferromagnetism above room temperature in nickel-tetracyanoethylene thin films, *J. Mater. Chem.* **19**, 6610 (2009).
- 31 D. Haskel, Z. Islam, J. Lang, C. Kmety, G. Srajer, K.I. Pokhodnya, A.J. Epstein, and J.S. Miller, Local structural order in the disordered vanadium tetracyanoethylene room-temperature molecule-based magnet, *Phys. Rev. B.* **70**, 054422 (2004).
- 32 N.P. Raju, V.N. Prigodin, K.I. Pokhodnya, J.S. Miller, and A.J. Epstein, High field linear magnetoresistance in fully spin-polarized high-temperature organic-based ferrimagnetic semiconductor V(TCNE)<sub>x</sub> films,  $x \sim 2$ , *Synth. Met.* **160**, 307 (2010).
- 33 V.N. Prigodin, N.P. Raju, K.I. Pokhodnya, J.S. Miller, and A.J. Epstein, Electronic Spin-Driven Resistance in Organic-Based Magnetic Semiconductor V[TCNE]<sub>x</sub>, *Synth. Met.* **135**, 87 (2003).

## References

---

- <sup>34</sup> K.I. Pokhodnya, D. Pejakovic, A.J. Epstein, and J.S. Miller, Effect of solvent on the magnetic properties of the high-temperature V[TCNE]<sub>x</sub> molecule-based magnet, *Phys. Rev. B* **63**, 174408 (2001).
- <sup>35</sup> J.B. Kortright, D.M. Lincoln, R.S. Edelstein, and A.J. Epstein, Bonding, Backbonding and Spin-Polarized Molecular Orbitals: Basis for Magnetism and Semiconducting Transport in V[TCNE]<sub>x-2</sub>, *Phys. Rev. Lett.* **100**, 257204 (2008).
- <sup>36</sup> C. Tengstedt, M.P. de Jong, A. Kanciurzevska, E. Carlegrim, and M. Fahlman, X-Ray Magnetic Circular Dichroism and Resonant Photoemission of V(TCNE)<sub>x</sub> Hybrid Magnets, *Phys. Rev. Lett.* **96**, 057209 (2006).
- <sup>37</sup> M.P. de Jong, C. Tengstedt, A. Kanciurzevska, E. Carlegrim, W.R. Salaneck, and M. Fahlman, Chemical bonding in V(TCNE)<sub>x</sub> (x~2) thin-film magnets grown in situ, *Phys. Rev. B* **75**, 064407 (2007).
- <sup>38</sup> C. Tengstedt, M. Unge, M.P. de Jong, S. Stafström, W.R. Salaneck, and M. Fahlman, Coulomb interaction in rubidium-doped tetracyanoethylene: a model system for organometallic magnets, *Phys. Rev. B* **69**, 165208 (2004).
- <sup>39</sup> P. Bhatt, E. Carlegrim, A. Kanciurzevska, M.P. de Jong, and M. Fahlman, Electronic structure of thin film iron-tetracyanoethylene: Fe(TCNE)<sub>x</sub>, *Appl. Phys. A* **95**, 131 (2009).
- <sup>40</sup> S.A. Wolf and D. Treger, Spintronics: A new paradigm for electronics for the new millennium, *IEEE Trans. Magn.* **36**, 2748 (2000).
- <sup>41</sup> S.A. Wolf, D.D. Awschalom, R.A. Buhrman, J.M. Daughton, S.V. Molnár, M.L. Roukes, A.Y. Chtelkanova, and D.M. Treger, Spintronics: A spin-based electronics vision for the future, *Science* **294**, 1488 (2001).
- <sup>42</sup> A. Wallerius, Elektronernas spinn styr framtidens elektronik, *Ny Teknik* nr **6**, 14 (2003).
- <sup>43</sup> S.A. Wolf, D. Treger, and A. Chtchelkanova, Spintronics: The future of data storage?, *MRS Bullet.* **31**, 400 (2006).
- <sup>44</sup> [http://nobelprize.org/nobel\\_prizes/physics/laureates/2007/phyadv07.pdf](http://nobelprize.org/nobel_prizes/physics/laureates/2007/phyadv07.pdf)  
Accessed April 15, 2010.
- <sup>45</sup> J. Camarero and E. Coronado, Molecular vs. inorganic spintronics: the role of molecular materials and single molecules, *J. Mater. Chem.* **19**, 1678 (2009).

## References

---

- 46 F. Wang and Z.V. Vardeny, Organic spin valves: the first organic spintronics devices, *J. Mater. Chem.* **19**, 1685 (2009).
- 47 G.A. Prinz, Magnetoelectronics, *Science* **282**, 1660 (1998).
- 48 A.J. Epstein and V.N. Prigodin, Polymer-, organic-, and molecular-based spintronic devices, US patent application 20030001154, 2003.
- 49 J.S. Miller and A.J. Epstein, Organic and Organometallic Molecular Magnetic Materials - Designer Magnets, *Angew. Chem. Int. Ed. Engl.* **33**, 385 (1994).
- 50 M.S. Thorum, K.I. Pokhodnya, and J.S. Miller, Solvent enhancement of the magnetic ordering temperature ( $T_c$ ) of the room temperature  $V(\text{TCNE})_x \cdot S$  ( $S$  = solvent, TCNE=tetracyanoethylene;  $x \sim 2$ ) magnet, *Polyhedron* **25**, 1927 (2006).
- 51 J.S. Miller, Organometallic- and organic-based magnets: new chemistry and new materials for the new millennium, *Inorg. Chem.* **39**, 4392 (2000).
- 52 M. Ohring, *Materials Science of Thin Films* (Academic Press, Boston, 2002).
- 53 P. van Zant, *Microchip fabrication: a practical guide to semiconductor processing* (McGraw-Hill, New York, 2000).
- 54 D. de Caro, M. Basso-Bert, J. Sakah, H. Casellas, J-P. Legros, L. Valade, and P. Cassoux, CVD-grown Thin Films of Molecule-Based Magnets, *Chem. Mater.* **12**, 587 (2000).
- 55 K.I. Pokhodnya, A.J. Epstein, and J.S. Miller, Thin-film  $V[\text{TCNE}]_x$  magnets, *Adv. Mater.* **12**, 410 (2000).
- 56 G.E. Muilenberg ed., *Handbook of X-ray photoelectron spectroscopy* (Perkin-Elmer Corporation, Minnesota, 1979).
- 57 L. Nemeč, L. Chia, and P. Delahay, Photoelectron spectroscopy of liquids: external ionization energies, *J. Electron Spectrosc. Relat. Phenom.* **9**, 241 (1976).
- 58 S. Hagström, C. Nordling, and K. Siegbahn, *Electron Spectroscopy for Chemical Analysis*, *Phys. Lett.* **9**, 235 (1964).
- 59 S. Hüfner, *Photoelectron spectroscopy: Principle and applications* (Springer Verlag, Berlin, 2003).

## References

---

- 60 C. Nordling, E. Sokolowski, and K. Siegbahn, *Precision method for  
obtaining absolute values of atomic binding energies*, *Phys. Rev.* **105**, 1676  
(1957).
- 61 W.R. Salaneck, S. Stafström, and J-L. Brédas, *Conjugated polymer surfaces  
and interfaces* (Cambridge University Press, Cambridge, 1996).
- 62 A. Zangwill, *Physics at surfaces* (Cambridge University Press, Cambridge,  
1988).
- 63 D. Briggs and M.P. Seah eds., *Practical Surface Analysis* (John Wiley and  
Sons, West Sussex, 1990).
- 64 N. Mårtensson and A. Nilsson, On the origin of core-level binding energy  
shifts *J. Electron Spectrosc. Relat. Phenom.* **75**, 209 (1995).
- 65 G. Wendin, *Breakdown of the one-electron picture in photoelectron spectra*  
(Springer-Verlag, New York, 1981).
- 66 D.W. Turner and M.L.A. Jobory, Determination of ionization potentials by  
photoelectron energy measurements, *J. Chem. Phys.* **37**, 3007 (1962).
- 67 C. Tengstedt, *Materials study of organic electronics*, Linköping University,  
2005.
- 68 D. Attwood, *Soft X-rays and extreme ultraviolet radiation* (Cambridge  
university press, Cambridge, 1999).
- 69 H. Winick and S. Doniach eds., *Synchrotron Radiation Research* (Plenum  
Press, New York, 1980).
- 70 <http://www.maxlab.lu.se> Accessed April 15, 2010.
- 71 J. Stöhr, *NEXAFS spectroscopy* (Springer-Verlag, Berlin, 1996).
- 72 P.A. Brühwiler, O. Karis, and N. Mårtensson, Charge-transfer dynamics  
studied using resonant core spectroscopies, *Rev. Mod. Phys.* **74**, 703 (2002).
- 73 L.A. Engström, *Elektromagnetism Från bärnsten till fältteori*  
(Studentlitteratur, Lund, 2000).
- 74 I. Soroka, *Magnetic heterostructures: the effect of compositional modulation  
of magnetic properties*, Uppsala University, 2005.
- 75 S. Felton, *Tunable magnetic properties of transition metal compounds*,  
Uppsala University, 2005.

- <sup>76</sup> R. Nyholm, J.N. Andersen, U. Johansson, B.N. Jensen, and I. Lindau, Beamline I311 at MAX-lab: a VUV/soft X-ray undulator beamline for high resolution electron spectroscopy, *Nucl. Instr. and Meth. in Phys. Res. A* **467**, 520 (2001).
- <sup>77</sup> <http://www.maxlab.lu.se/beamline/max-ii/d1011/d1011.html> Accessed April 15, 2010.
- <sup>78</sup> S.K.M. Jönsson, E. Carlegrim, F. Zhang, W.R. Salaneck, and M. Fahlman, Photoelectron spectroscopy of the contact between the cathode and the active layers in plastic solar cells, *Jpn J. Appl. Phys.* **44**, 3695 (2005).
- <sup>79</sup> N. Ueno, H. Fujimoto, N. Sato, K. Seki, and H. Inokuchi, Angle-Resolved Photoemission from Oriented Thin Films of Long Alkyl Molecules: Valence Band Dispersion, *Phys. Scr.* **41**, 181 (1990).
- <sup>80</sup> K. Seki, N. Ueno, U.O. Karlsson, and R. Engelhardt, Valence bands of oriented finite linear chain molecular solids as model compounds of polyethylene studied by angle-resolved photoemission, *Chem. Phys.* **105**, 247 (1986).
- <sup>81</sup> C.K. Chiang, C.R. Fincher, Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis, S.C. Gau, and A.G. MacDiarmid, Electrical Conductivity in Doped Polyacetylene, *Phys. Rev. Lett.* **39**, 1098 (1977).
- <sup>82</sup> J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Makay, R.H. Friend, P.L. Burn, and A.B. Holmes, Light emitting diodes based upon conjugated polymers, *Nature* **347**, 539 (1990).
- <sup>83</sup> A.J. Heeger, Semiconducting and Metallic Polymers: The Fourth Generation of Polymeric Materials (Nobel Lecture), *Angew. Chem. Int. Ed.* **40**, 2591 (2001).