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Preparation and characterization of an organic-based magnet

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Abstract

In the growing field of spintronics there is a strong need for development of flexible lightweight semi-conducting magnets. Molecular organic-based magnets are attractive candidates since it is possible to tune their properties by organic chemistry, making them so-called “designer magnets”. Vanadium tetracyanoethylene, $V(TCNE)_x$, is particularly interesting since it is a semiconductor with Curie temperature above room temperature ($T_C \sim 400$ K). The main problem with these organic-based magnets is that they are extremely air sensitive. This thesis reports on the frontier electronic structure of the $V(TCNE)_x$ by characterization with photoelectron spectroscopy (PES) and near edge x-ray absorption fine structure (NEXAFS) spectroscopy. It also presents a new and more flexible preparation method of this class of organic-based thin film magnets. The result shows improved air stability of the $V(TCNE)_x$ prepared with this method as compared to $V(TCNE)_x$ prepared by hitherto used methods.

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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

Submitted

Author's contribution: All the experimental work and data analysis in co-operation. Wrote the first draft and was responsible for the iterative process to the final version.

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

Manuscript

Author's contribution: All the experimental work and data analysis in co-operation. Wrote the first draft and was responsible for the iterative process to the final version.

Paper III

A new preparation method resulting in more air-stable $V(\text{TCNE})_2$; a semi-conducting room temperature molecular magnet

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Related papers and patent 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

Jpn J. Appl. Phys., **44**, 3695, 2005.

X-ray magnetic circular dichroism and resonant photoemission of V(TCNE)_x hybrid magnets

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

Phys. Rev. Lett., **96**, 057209/1, 2006.

Chemical bonding in V(TCNE)_x (x~2) thin-film magnets grown *in situ*

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

Phys. Rev. B, **75**, 64407-1, 2007.

Electronic structure of Fe(TCNE)_x thin film magnets

P. Bhatt, E. Carlegrim and M. Fahlman

Manuscript

Process of producing organomagnetic materials

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

Patent pending

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1 Introduction

Magnets based on organic materials, so-called organic-based molecular magnets (OMMs), is a new and ‘exotic’ field of organic electronics.¹ 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 properties can be tuned by molecular design.²⁻⁴ Other advantages include conductivity ranging from semi-conducting to insulating, low weight, low temperature processing, low environmental contamination etc.²⁻⁴ Some organic-based magnets also offer properties not seen in conventional magnets, such as light-induced magnetism,⁵ solubility in organic solvents and biocompatibility.²⁻⁴ The belief in that organic magnets could exist was of theoretical nature, formulated in the 1950s, and it took until the mid 1980s until the first organic-based magnets were prepared.⁶ A breakthrough came 1991 when the first room temperature organic-based magnet was discovered,⁷ opening the door to many potential applications. In the same year also the first purely organic magnets were discovered.^{8, 9} Once those materials are well characterized, they may very well be used in both traditional applications and applications not thought of yet. Room temperature organic-based magnets could eventually be used in functional coatings such as frequency or magnetic shielding and anti-static coatings.¹⁰ One can also imagine less traditional applications in so-called spin-based electronics (spintronics),¹¹ 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 three included papers. The introductory part provides an overview of organic-based magnets, their preparation methods and some of the experimental techniques for studying OMMs. It also contains a presentation

of the equipment utilized for the work in this thesis. **Paper I** relates to the studies of the frontier unoccupied electronic structure of the semi-conducting room temperature organic-based magnet vanadium tetracyanoethylene, $V(TCNE)_x$, by using a model system of this compound. **Paper II** is a continuation of the first paper and studies of sodium-doped $V(TCNE)_x$ enables determination of the lowest unoccupied molecular orbital (LUMO) of $V(TCNE)_x$. In **Paper III** a new preparation method of organic-based magnets is presented, enabling for the first time preparation of relatively air-stable $V(TCNE)_x$.

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).² One of the most extensively studied family of 3D organic-based magnets is transition-metal tetracyanoethylene complexes, $M(\text{TCNE})_x$.^{7, 12-14} 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.⁷ The main focus in this thesis is $V(\text{TCNE})_x$ and its properties are discussed in the last paragraph of this chapter.

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, the magnetic ordering only occurs below a critical temperature, the so-called Curie temperature of ferro- and ferrimagnets or Néel temperature of antiferromagnets.^{15, 16}

2.1.1 Magnetic ordering

The interaction of spins at nearby sites leads to different spin configurations, namely, para-, ferro-, antiferro- and ferrimagnetism. In a paramagnet the spins are aligned in different directions and those directions are changed 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. Ferrimagnetism is a special case of antiferromagnetism and below the Curie 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 are not a property of an individual molecule, they are bulk properties. In some materials the direction of the spins locally freezes and their orientation is changed extremely slowly with respect to time below a certain temperature. This behavior is called spin glass² and is commonly occurring in organic-based magnets, e.g. in $V(\text{TCNE})_x$ prepared in solution (see chapter 3).

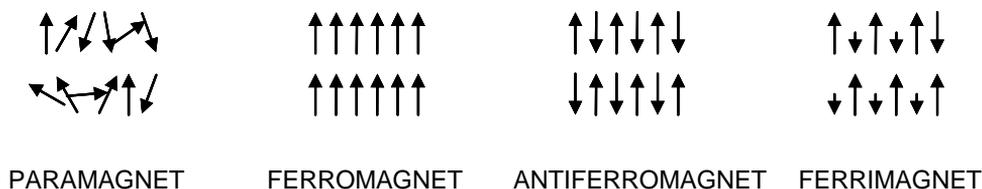


Figure 2.1 Examples of different spin configurations in absence of an external field.

2.1.2 Magnetic interactions

There are two types of magnetic interactions, Heisenberg exchange interaction and dipole-dipole interaction, respectively.^{2,3} The Heisenberg effect is a quantum effect and is due to the Pauli's exclusion principle, while the classical dipole-dipole interaction effect occurs between two magnetic dipoles. Since the Heisenberg effect (in most cases) dominates, the dipole-dipole effect is generally neglected. The pair-wise spin interaction in (ferro- and antiferro-) magnetic systems at zero applied magnetic field may be described by the Heisenberg Hamiltonian:

$$H = -2 \sum_{i,j} J_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j \quad (2.1)$$

where i and j are independent of directions (x, y or z) of the nearest-neighbor sites and $\mathbf{S}_i \cdot \mathbf{S}_j$ 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. Since organic-based magnets often are disordered, a term representing random magnetic anisotropy (see paragraph below) is sometimes included into the equation:

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

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.²

2.1.3 Magnetic disorder

The main factors influencing the type of magnetic ordering are spin dimensionality, lattice dimensionality, spin value, disorder and frustration. Magnetically ordered amorphous solids, e.g. hybrid organic-inorganic compounds, show magnetic random anisotropy, 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 the network, simultaneously. This leads to peculiar magnetic phenomena at low temperatures, e.g. spin glass state.^{2,3}

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 strength of magnetization of a magnetic material. When the coercive field of a magnet is large, the material is said to be hard, 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.¹⁶

2.2 Materials

$M(\text{TCNE})_x$, where $M = \text{V, Fe, Mn, Co, Ni}$ etc., TCNE = tetracyanoethylene, $x \sim 2$,^{7, 12-14},¹⁷ is one of the most studied family of organic-based magnets. Recently, it has been extended to also include Cr, Nb and Mo.¹⁸ As can be realized, an unlimited number of variants of $M(\text{TCNE})_x$ can be prepared by exchanging the metal or the organic molecule,¹⁹⁻²¹ as well as both. Combination of metals, i.e. $M^z M^{z'}_{1-z}(\text{TCNE})_x$, $0 < z < 1$, has also been reported,^{17, 22, 23} some showing Curie temperatures above room temperature. Moreover, the stoichiometry of

the present species can be varied, e.g. such that x deviates from 2, while still obtaining magnetic ordering above room temperature.²⁴

Particularly $V(\text{TCNE})_x$ has caught the interest since it was the first room temperature (T_C is close to 400 K) organic-based magnet when reported in 1991.⁷ Unfortunately, the material is extremely air sensitive and this, together with its disordered structure, has hindered the study 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, only thin films are considered.

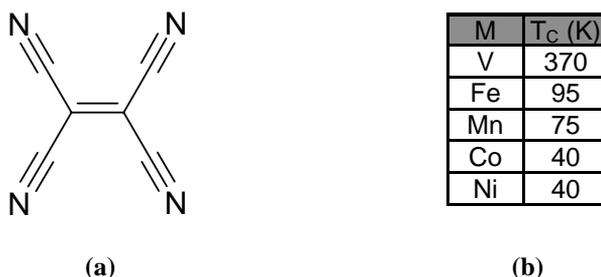


Figure 2.2 (a) The chemical structure of TCNE. (b) Curie temperatures of different $M(\text{TCNE})_x$.^{7, 12-14, 17}

In $V(\text{TCNE})_x$, 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.²⁵

In contrast to transition- and rare-earth-based metallic magnets, $V(\text{TCNE})_x$ is semiconductor with a conductivity of about 10^{-4} Scm^{-1} at room temperature. It decreases with decreasing temperature, which suggests a hopping transport mechanism.²⁶ A low coercive field of about 4.5 Oe has been reported at room temperature, characteristic of a soft magnet.²⁷

In 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, Δ , a well-known property of 3d elements. The highest occupied molecular orbital (HOMO) is mainly localized on the $V(3d)$ units and is characterized by strong hybridization between $V(3d)$ and the TCNE^- units.^{28, 29} The lowest unoccupied molecular orbital (LUMO) is localized on the TCNE^- units as will be shown by this thesis (see paper I and paper II). When adding an extra electron to a small system, such as $V(\text{TCNE})_x$, a Coulomb gap around the Fermi level is created.³⁰ 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.

The coupling between the 3/2 spin on V^{2+} and 1/2 spin on the two $TCNE^-$ is proposed to be antiferromagnetic, yielding a ferrimagnetic state and hence a net spin of 1/2 for $V(TCNE)_2$. Magnetotransport measurement of $V(TCNE)_x$ thin films have demonstrated positive magnetoresistance,²⁶ i.e. increase in resistance with applied field. At room temperature and an applied field of 6 kG, the resistance was increased 0.7% which is almost three orders of magnitude larger than what is predicted for a disordered semiconductor.⁴ This anomalously large magnetoresistance was explained by a model where the π^* -band is split into two subbands, one occupied and one unoccupied, with opposite spin polarization. From this model it is proposed that $V(TCNE)_x$ can be described as a fully spin-polarized, half-semiconductor.²⁶ No experimental evidence for the proposed valence electronic structure existed, and later, it has been shown that the HOMO actually is $V(3d)$ -derived (as described above), and not $TCNE^-$ π^* -derived. Apart from that, the rest of the model is still valid, as will be shown by this thesis. The semi-conducting behavior at room temperature and the fully spin-polarized charge transport (half-conducting state) are desirable properties in spintronic applications (see paragraph, below).

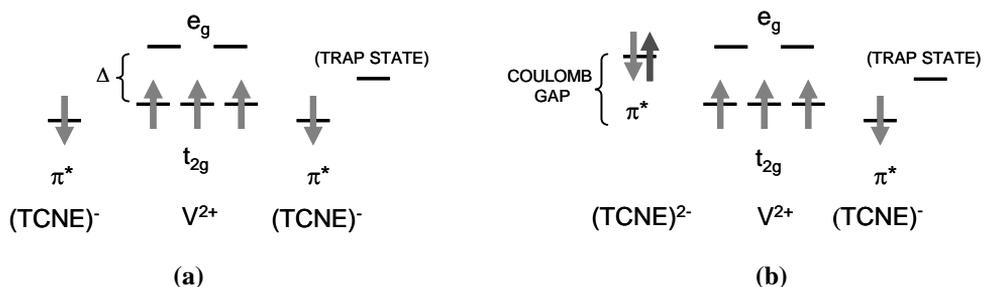


Figure 2.3 Frontier electronic structure of $V(TCNE)_2$. (a) Ground state. (b) With one extra electron added.

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. Instead, they may find their own niches since they have exposed properties never associated with magnets before, such as bistability (e.g. light-induced magnetism), transparency and potentially biocompatibility.^{2, 4} One of the most promising applications of OMMs is in the new field spintronics,^{31, 32} also known as magnetoelectronics. Spintronics is the abbreviation for spin transport electronics and as the

name implies, these devices utilize not only the charge of the electron as information carrier, but also its spin direction, “spin up” or “spin down”. Advantages of using the electron spin as information carrier include, faster data processing speeds, non-volatility and less electrical power consumption. Examples of (potential) spintronic applications are spin-valves, spin-based light-emitting devices and spin-based field effect transistors etc.^{31, 32} To date, the most successful spintronic device is the spin valve.

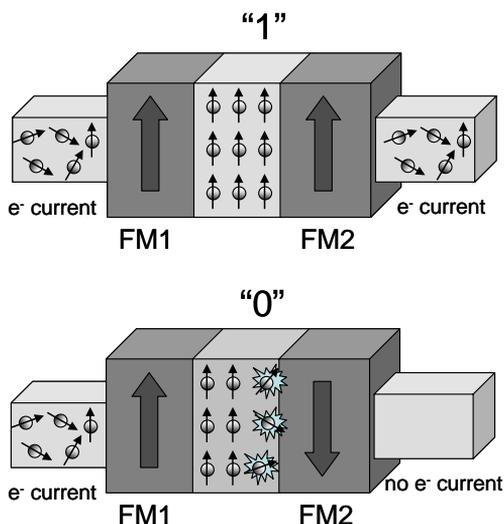


Figure 2.4 The principle of a spin valve device. Low resistance gives “1” and high resistance gives “0”, respectively. The magnetic field is denoted by the large arrows. The spacer (light grey) is sandwiched between two ferromagnetic (FM) materials, one with fixed magnetization (FM1) and one with tunable magnetization (FM2).

The principle of a spin valve is that a non-magnetic material is spaced between two layers of ferromagnetic metal.³³ One of the two magnetic layers has to have 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, which was rewarded the Nobel prize this year (2007).³⁴ An example of an inorganic spintronic device, already commercialized, is the read head for hard disk drivers, which nowadays can 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. Organic materials exhibit advantages, such as mechanically flexibility, low temperature and potential low-cost device fabrication, tunability of the properties via chemical routes etc.⁴ In addition, light elements have weak spin-orbit coupling and low hyperfine interaction, leading to longer spin-coherence times and longer spin-coherence lengths as compared to inorganic materials. The first organic-based spintronic device was reported in 1998³⁵ and 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.

3 Preparation methods

Organic-based molecular magnets have shown to be capricious to prepare and reproduce. In this chapter the main focus is the different preparation methods of organic-based magnets in the $M(\text{TCNE})_x$ family and especially $V(\text{TCNE})_x$. The most common method for preparation of organic-based magnets in the $M(\text{TCNE})_x$ family is chemical synthesis, which leads to an insoluble magnetic powder. A few years ago a new preparation method was reported, resulting in thin film formation of the material.

3.1 Solution-based preparation

The first and most frequently used method for preparation of all organic-based molecular 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 (leading to substantially lower Curie temperatures of the magnets) or non-coordinating.^{27, 36} For preparation of $V(\text{TCNE})_x$, the precursors are TCNE and bis(benzene)vanadium,⁷ $V(\text{C}_6\text{H}_6)_2$, or vanadium hexacarbonyl,²⁷ $V(\text{CO})_6$. When the reaction has taken place, the resulting precipitate is filtrated and dried under vacuum, forming an amorphous insoluble magnetic powder.³⁷ Magnets prepared by this method always contain residual solvent molecules and by-products from the precursors. This causes disorder in the material and therefore $V(\text{TCNE})_x$ prepared by chemical synthesis is extremely air sensitive and decomposes after only a few seconds in air, sometimes in a pyrophoric manner.⁷

3.2 Chemical vapor deposition (CVD)

Chemical vapor deposition (CVD) 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. 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. The main drawback of CVD processes is the use of often toxic, corrosive and/or flammable precursors.^{18, 38, 39}

Processing by chemical vapor deposition (CVD) was the first step towards applications of $V(\text{TCNE})_x$ since the method produces thin films. As these thin films are solvent-free, the deleterious effect of the solvent is eliminated, resulting in enhanced stability and magnetic properties of the magnets, as compared to the synthesized ones.⁴⁰ Apart from $V(\text{TCNE})_x$, also $M(\text{TCNE})_x$, where $M = \text{Cr}, \text{Nb}$ and Mo have been prepared by the CVD-based technique.¹⁸ As the synthesized magnets, the thin film magnets produced by this CVD-based method contains substantially amounts of oxygen.⁴⁰ The first completely oxygen-free $V(\text{TCNE})_x$ thin films were prepared by an *in-situ* ultra-high vacuum (UHV) compatible CVD method.^{28, 29} In this process, $V(\text{C}_6\text{H}_6)_2$, and TCNE are allowed to react in the vacuum chamber and no carrier gas is used to transport the precursors. This *in-situ* preparation also allows for usage of more sophisticated surface-sensitive methods for characterization of e.g. the electronic structure and magnetic properties. By the use of CVD the negative effect of residual solvents is eliminated, however the problem with residual by-products from the reaction still remains.

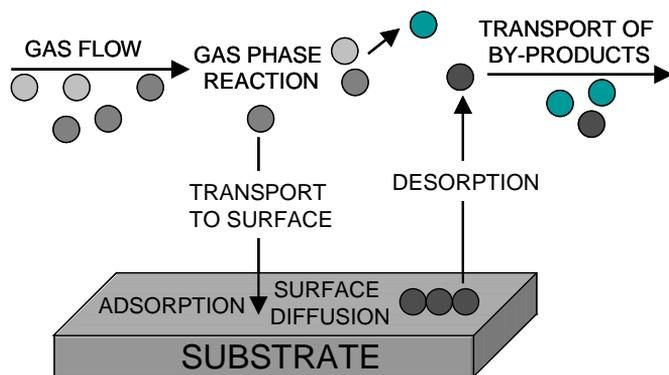


Figure 3.1 A schematic picture of the steps involved in the CVD process.

3.3 Physical vapor deposition (PVD)

Physical vapor deposition (PVD) is a general term for 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, leading to a more clean process than the CVD counterpart.³⁸

We developed the PVD-based process for preparation of $M(\text{TCNE})_x$ thin films 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. 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[®] EFM3 UHV e-beam evaporator, and a gas handling system providing the organic molecules. This portable set-up can be mounted on any (ultrahigh-) vacuum system, allowing for *in-situ* preparation and characterization of the thin film magnets. By using PVD-deposition of a metal one can avoid the often hazardous and very reactive metal-organic precursor. The PVD-based method is therefore much more flexible, since high purity metals, in contrast to the organic-metallic precursors, are commercially available. 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. The first result on $V(\text{TCNE})_x$ prepared by this method shows much improved air stability of the compound as compared to $V(\text{TCNE})_x$ prepared by chemical synthesis or CVD (see paper III).

4 Experimental techniques

Photoelectron spectroscopy (PES) and near edge x-ray absorption fine structure (NEXAFS) spectroscopy are two techniques well suited for studies of the occupied and unoccupied electronic structure, respectively, 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. The technique is based on the photoelectric effect which was discovered by Hertz in 1887 and explained theoretically by Einstein in 1905. 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. Photoelectron spectroscopy is often referred to as a fingerprint technique since each element has its unique PES pattern. In addition, many chemical and physical properties of a sample can be obtained by the technique.^{41, 42}

4.1.1 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.⁴¹ The ejected photoelectrons are collected and detected by a system comprising of electromagnetic 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 is given, from the law of conservation, by the equation below:

$$E_B = h\nu - E_{kin} \quad (4.1)$$

PES is a very surface sensitive method, which is due to the small mean free path (MFP) 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). 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.⁴¹

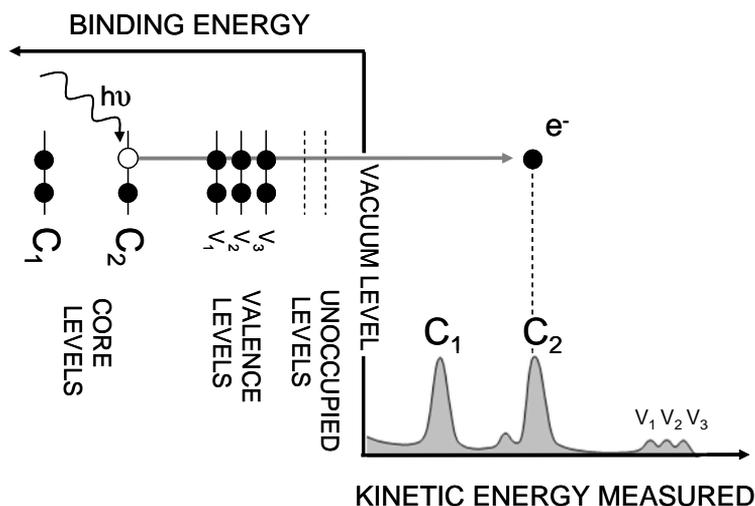


Figure 4.1 A schematic figure of a photoelectron spectrum and its correspondence to the ionization of various energy levels.

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 are studied by UV photoelectron spectroscopy (UPS) which is even more surface sensitive with only the first few monolayers (ca 15-20 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. 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.⁴³

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 energies this allow 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.⁴⁴ 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 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),⁴² which provide appropriate scaling of the photoelectron peaks. The ASF consider factors, 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:

$$I = I_0 \exp\left(\frac{-d}{\lambda}\right) \quad (4.2)$$

where d is the film thickness, I_0 is the original signal, I is the attenuated signal and λ is the MFP.⁴³

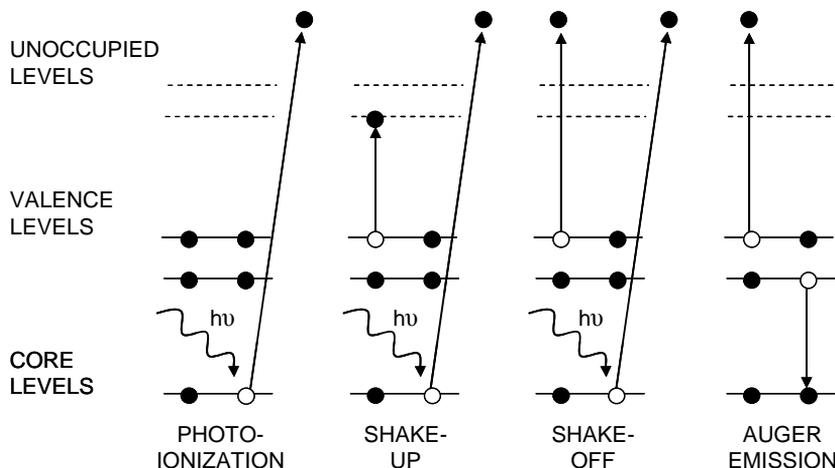


Figure 4.2 A schematic figure of some possible electron emitting processes, namely photoionization (from a core level), shake-up, shake-off and Auger emission.

Apart from photoelectron peaks which are the most narrow and intense peaks in a PES spectrum, there are 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. Different screening effects give rise to different excited states (each with its own probability). Fig. 4.2 illustrates examples of some final state effects, namely photoionization, shake-up, shake-off and Auger emission.⁴⁵ 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.

4.1.3 Valence level spectroscopy (UPS)

The density of occupied electronic states in the valence band region is commonly studied by ultraviolet photoelectron spectroscopy. A UPS spectrum also provides information needed for determination of important parameters of a sample, such as the ionization potential or work function. The work function, ϕ_s , can be derived from:

$$\phi_s = E_{vac} - E_F = h\nu - E_{CO} \quad (4.3)$$

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.

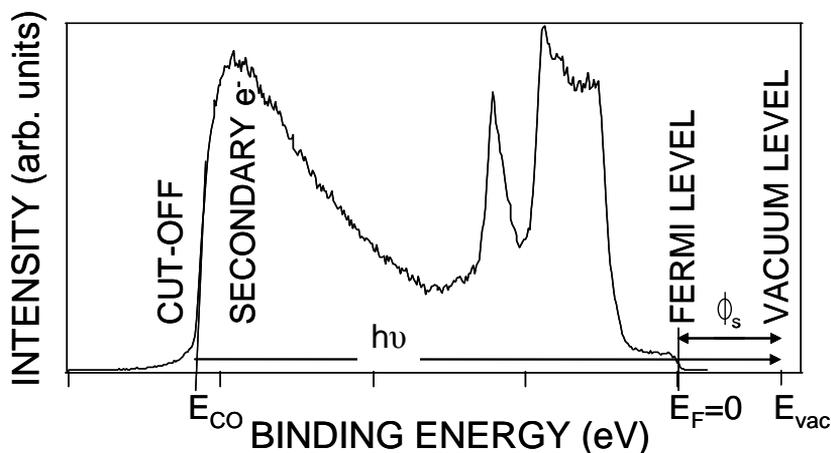


Figure 4.3 A HeI spectrum of gold pointing out some of the information that can be obtained from UPS.

UPS is a suitable technique for e.g. studies of work function and valence feature changes upon the early stages of doping.

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 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.⁴³ The photoionization equation for a solid sample can hence be written:

$$h\nu = E_B^F + E_{kin} + \phi_{sp} \quad (4.4)$$

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

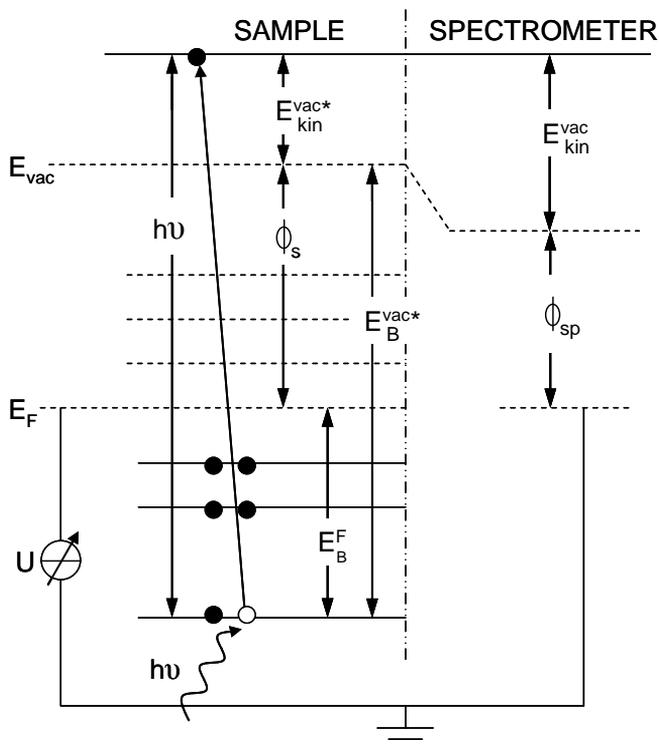


Figure 4.4 Energy level diagram of a sample in electrical contact with the spectrometer.

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.⁴³ Compensation can be done by an electron flood gun, 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. 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 a reference.

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 charging can also affect the widths of the peaks.⁴¹

4.2 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. 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. Therefore an absorption is followed by a dramatically increase of the number emitted electrons. Furthermore, the electron yield can be performed in two different ways, namely total yield and partial yield. 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. NEXAFS can also be used for studying the orientation of the molecules by measuring the sample at different rotations (relative to the analyzer).⁴⁶

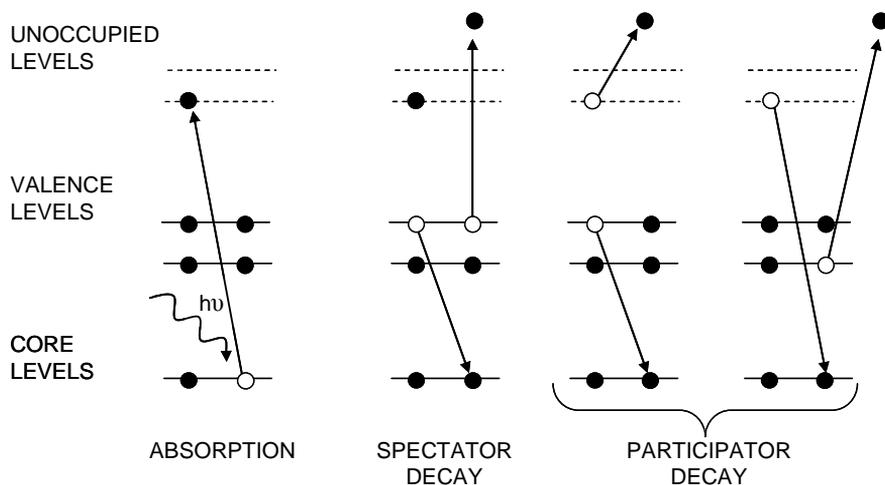


Figure 4.5 Principle of absorption and the following Auger processes (decay channels).

4.3 Photon sources

Photon sources can be either fixed or tunable. 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. The electrons create holes in the anode, 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.⁴¹

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, they emit electromagnetic radiation. The energy of the synchrotron light 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 XPS or NEXAFS. Other characteristics of synchrotron radiation include high photon flux,

brightness, brilliance and polarized light. 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, is located in Lund, Sweden.^{47, 48}

4.4 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). 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 basic element of a SQUID is a superconducting ring containing two Josephson junctions. When a sample is passed through the ring, the induced current is proportional to the magnetization of the sample.^{49, 50}

5 Equipment

The work presented in this thesis has been performed at the two photoelectron spectrometers “Scienta” and “Moses” in the Surface Physics and Chemistry Laboratory at Linköping University. Additional measurements were performed at the Swedish national synchrotron laboratory, MAX-lab 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 three vacuum chambers namely, introduction, preparation and analysis chamber.

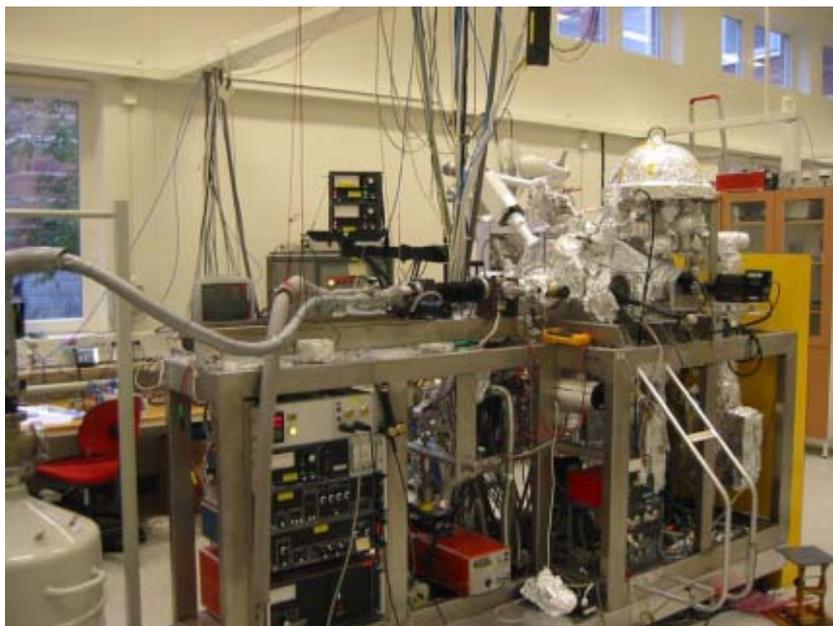


Figure 5.1 The custom-built photoelectron spectrometer “Moses”.

The analysis chamber is equipped with a nonmonochromatized x-ray source ($h\nu$: $\text{AlK}_{\alpha} = 1486.6$ eV) and a monochromatized helium discharge lamp ($h\nu$: $\text{HeI} = 21.2$ eV and $\text{HeII} = 40.8$ 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.

5.2 Scienta

The commercially available Scienta® ESCA 200 spectrometer equipped with a hemispherical analyzer combined with a multi-channel plate 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 ($h\nu$: $\text{AlK}_{\alpha} = 1486.6$ eV) and a helium discharge lamp providing non-monochromatized helium light ($h\nu$: $\text{HeI} = 21.2$ eV and $\text{HeII} = 40.8$ eV).

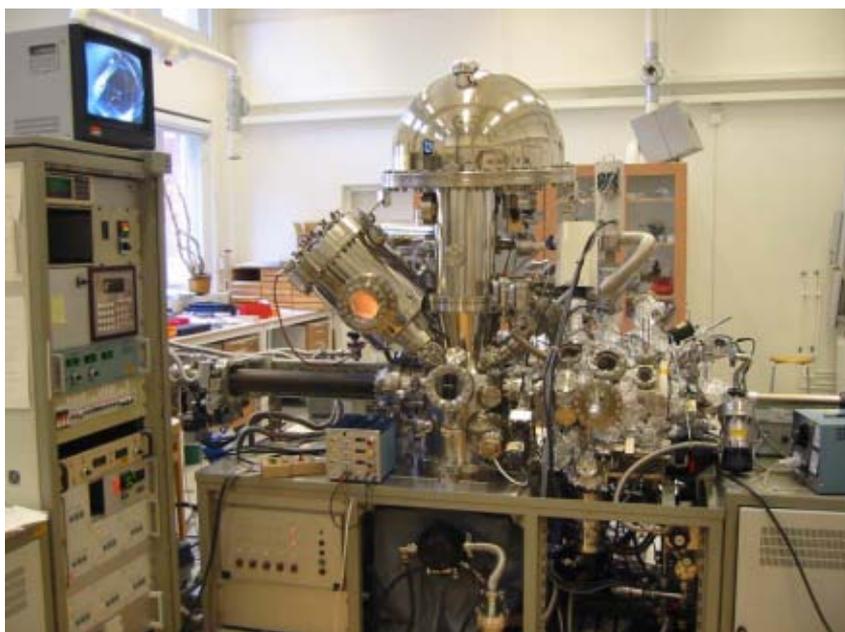


Figure 5.2 The Scienta® ESCA 200 photoelectron spectrometer.

The preparation chamber is equipped with an ion sputter gun for preparation of ultra-clean surfaces, free ports where deposition sources, such as the Omicron[®] 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 °C to 300 °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.

5.3 Beamline I311

The undulator-based beamline I311⁵¹ is located at the third generation 1.56 GeV storage ring MAX II at the Swedish national laboratory, MAX-lab,⁴⁷ 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 XPS and NEXAFS. This end station is equipped with a Scienta[®] 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.



Figure 5.3 Beamline I311 at MAX-lab.

6 Summary

In this last chapter, a short summary of how the work presented in this thesis have contributed to the field of organic-based magnets, especially vanadium tetracyanoethylene, $V(TCNE)_x$,⁷ is given. $V(TCNE)_x$ is a magnetic semiconductor with spin-polarized valence and conduction bands, suggesting spintronic applications.²⁶ Unfortunately, it is extremely air sensitive which has hampered the development of the material. Our group recently reported on preparation of completely oxygen-free $V(TCNE)_x$, via an *in-situ* ultra-high vacuum compatible method, based on chemical vapor deposition (CVD).^{28, 29} The CVD-based method has been utilized for preparation of $V(TCNE)_x$ in the first two papers.

Starting with **Paper I**, a model system of $V(TCNE)_x$, enabled the determination of the nature of the frontier unoccupied electronic structure of $V(TCNE)_x$. In contrast to the occupied electronic structure,^{28, 29} which is strongly hybridized, there is no (or very little) hybridization between vanadium and TCNE in the unoccupied frontier electronic structure, leading to that the lowest unoccupied molecular orbital (LUMO) is either localized on vanadium *or* on TCNE. In **Paper II**, the work regarding the frontier unoccupied electronic structure of $V(TCNE)_x$ was continued, resulting in a more complete picture of the frontier electronic structure of the material. By Na-doping of $V(TCNE)_x$ it was possible to determine the location of the LUMO to the TCNE⁻-derived states. This study also showed that there are trap states for electron transport present in the material, most likely originating from residual by-products from the preparation process. The results obtained from Paper I and Paper II have strong implication for use of $V(TCNE)_x$ in devices, as the frontier electronic structure is highly important for the charge transport and magnetic properties.

In order to use organic-based magnets in devices, less air sensitive materials have to be developed. In **Paper III** a new preparation method (patent pending), based on physical vapor deposition (PVD), of organic-based magnets is presented. The goal with this method is to prepare less disordered materials without contaminations from any by-products. The first study of $V(TCNE)_x$ prepared by this technique showed improved air stability as compared the material prepared by previously reported methods. Further, the method is much more flexible

since pure metal is used instead of the often hazardous and not always commercially available precursors.

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