



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

E. Carlegrim<sup>a</sup>, Y. Zhan<sup>a</sup>, M.P. de Jong<sup>b</sup>, M. Fahlman<sup>a,\*</sup>

<sup>a</sup> Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden

<sup>b</sup> MESA<sup>+</sup> Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands

### ARTICLE INFO

#### Article history:

Received 27 September 2010

Received in revised form 14 June 2011

Accepted 20 June 2011

Available online 20 July 2011

#### Keywords:

Organic magnets

Photoelectron spectroscopy

Near edge X-ray absorption fine structure

### ABSTRACT

$\text{V}(\text{TCNE})_x$ , TCNE = tetracyanoethylene,  $x \sim 2$ , is a semiconducting organic-based magnet and one of very few organic-based magnets with critical temperature above room temperature (RT). With the aim to understand the key design criteria for achieving RT organic-based magnets we have started to study the electronic and chemical structure of members of the  $\text{M}(\text{TCNE})_x$  family with significantly lower critical temperatures than  $\text{V}(\text{TCNE})_x$ . In this paper,  $\text{Co}(\text{TCNE})_x$ ,  $x \sim 2$ , ( $T_C \sim 44$  K, derived from its powder form) were prepared by a method based on physical vapor deposition, resulting in oxygen-free thin films. By using a variety of photoemission and X-ray absorption techniques the highest occupied molecular orbital (HOMO) of  $\text{Co}(\text{TCNE})_x$  was determined to mainly be  $\text{TCNE}^-$ -derived while the states originating from  $\text{Co}(3d)$  are localized at higher binding energies. This is in stark contrast to  $\text{V}(\text{TCNE})_x$  where  $\text{V}(3d)$  is mainly responsible for the HOMO, but in line with the results of  $\text{Fe}(\text{TCNE})_x$  ( $T_C \sim 121$  K, derived from its powder form) for which the HOMO also is  $\text{TCNE}^-$ -derived. Moreover, the results propose  $\text{Co}(\text{TCNE})_x$  to contain large amounts of local bonding disorder in contrast to  $\text{V}(\text{TCNE})_x$  which can be grown virtually defect free. We speculate that cobalt binds to vinyl – instead of cyano groups, hence creating a disordered bonding arrangement which deviates from octahedral. The very weak ( $<1$  eV) crystal field splitting and a large spread in the local ligand field strengths due to disorder in  $\text{Co}(\text{TCNE})_x$  are in agreement with the absence of fine structure in the Co L-edge spectra.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

The discovery of room temperature (RT) magnetism ( $T_C \sim 400$  K) [1] in vanadium tetracyanoethylene,  $\text{V}(\text{TCNE})_x$ , generated extensive interest in organic-based magnets of the  $\text{M}(\text{TCNE})_x$ ,  $\text{M} = \text{V}, \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$ , etc.,  $x \sim 2$ , family [2] which recently has been extended to also include Cr, Nb and Mo [3].  $\text{V}(\text{TCNE})_x$  is semiconducting [4] and has fully spin-polarized transport levels with the highest occupied molecular orbital (HOMO) of  $\text{V}(\text{TCNE})_x$  mainly localized on the vanadium sites while the lowest unoccupied molecular orbital (LUMO) is  $\text{TCNE}^-$  derived [5,6]. The coupling between  $\text{V}^{2+}$  and the two  $\text{TCNE}^-$  units is antiferromagnetic yielding a ferrimagnetic state and hence a net spin of 1/2 for each  $\text{V}(\text{TCNE})_x$  entity [7]. Each vanadium ion is coordinated to six cyano groups in a slightly distorted octahedral environment and the distribution of V–N bond lengths is small due to strong bonding between vanadium and TCNE [8]. The properties of  $\text{V}(\text{TCNE})_x$  make it potentially appealing for spintronic devices, e.g. spin valves.  $\text{V}(\text{TCNE})_x$  can be used as the soft ferromagnetic (FM) contact in a FM1/organic semiconductor/FM2 spin valve design [9]. Recently we proposed another spin valve design based on  $\text{V}(\text{TCNE})_x$ , where it instead is used as organic semiconducting

layer sandwiched between the two FM contacts [10]. This device make use of the fully spin-polarization and would operate in two different modes, either with two different FM contacts (one hard and one soft) or with two identical FM contacts.

Realization of such devices is complicated, however, and one of the main obstacles has been the preparation of the compound. When  $\text{V}(\text{TCNE})_x$  was first reported in 1991 [1], it was prepared in solution forming an insoluble, extremely air sensitive powder which contained both residual solvent molecules and residuals/by-products from the precursors (e.g. bis(benzene)vanadium,  $\text{V}(\text{C}_6\text{H}_6)_2$  or vanadium hexacarbonyl,  $\text{V}(\text{CO})_6$ ). Presence of small amounts of contamination and/or disorder may affect both the magnetic properties [11,12] and the electronic properties [6] of the material negatively. A huge step forward was made when  $\text{V}(\text{TCNE})_x$  was prepared as thin films by a chemical vapor deposition (CVD) route [13,14]. Although the material was free from residual solvent molecules, such films still contained precursor residuals/by-products and oxygen-induced defects. Therefore an *in situ* method, based on CVD as well but compatible with any ultra-high vacuum system was developed to avoid oxidation problems and enable device fabrication [5]. This CVD-based method allowed for completely oxygen-free  $\text{V}(\text{TCNE})_x$  thin films to be fabricated, but the method produces magnets which still may contain small amounts of residuals from the bis(benzene)vanadium,  $\text{V}(\text{C}_6\text{H}_6)_2$ , precursor. In order to also get rid

\* Corresponding author. Tel.: +46 13 28 1206; fax: +46 13 13 7568.

E-mail address: [mafah@ifm.liu.se](mailto:mafah@ifm.liu.se) (M. Fahlman).

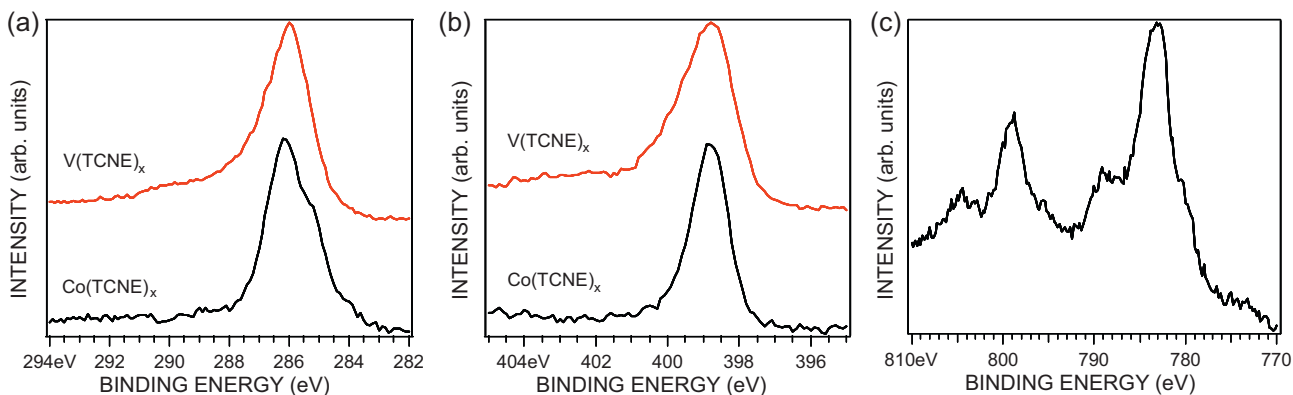


Fig. 1. Core level spectra of  $\text{Co(TCNE)}_x$  and  $\text{V(TCNE)}_x$ . (a) C(1s), (b) N(1s), and (c) Co(2p).

of the precursor residuals an additional method, based on physical vapor deposition (PVD), was developed which results in oxygen-free  $\text{M(TCNE)}_x$ , neither containing residual solvent nor precursors (or by-products thereof) [15] since only pure metals and TCNE are used in the preparation process. The PVD process produces films more resistant to oxidation, but the outermost surface of  $\text{V(TCNE)}_x$  films will always be highly reactive due to the  $\text{V}^{2+}$  sites present. Hence, though  $\text{V(TCNE)}_x$  has been developed to the point where it is an interesting material for pursuing research on device physics, its commercial potential will depend on the effectiveness of sealing the devices from atmospheric contaminants (i.e. water and oxygen).

Substituting  $\text{V}^{2+}$  by a less reactive ion would greatly enhance the viability of using the hybrid organic magnets in devices, but few alternatives show RT magnetic ordering. In order to try to develop an understanding on what are the key design criteria for achieving critical temperatures above RT, we have begun to synthesize and study  $\text{M(TCNE)}_x$  films that *do not* show RT magnetic ordering and comparing their chemical and electronic structure with that of  $\text{V(TCNE)}_x$ .  $\text{Fe(TCNE)}_x$  and  $\text{Co(TCNE)}_x$  were selected due their low critical temperatures,  $T_C \sim 121$  K and  $T_C \sim 44$  K respectively (values derived from their powder forms) [2]. We have shown in a previous paper that the HOMO of  $\text{Fe(TCNE)}_x$  is mainly localized on  $\text{TCNE}^-$  units in contrast to the case of  $\text{V(TCNE)}_x$  and that the crystal field parameter of  $\text{Fe(TCNE)}_x$ ,  $10Dq \sim 0.6$  eV [16], also differs as compared to  $\text{V(TCNE)}_x$  where  $10Dq \sim 2.3$  eV [17]. The weaker crystal field parameter and the drastically different frontier valence electronic structure was proposed to explain the substantially lower magnetic ordering temperature of  $\text{Fe(TCNE)}_x$  as compared to  $\text{V(TCNE)}_x$ . Herein, we present the first study on the electronic structure of  $\text{Co(TCNE)}_x$ , using a variety of photoemission and X-ray absorption techniques. The results are compared with the previously results on  $\text{V(TCNE)}_x$  and  $\text{Fe(TCNE)}_x$ .

## 2. Experimental

Thin films of  $\text{Co(TCNE)}_x$  were prepared on Au substrates at room temperature by a method based on physical vapor deposition. The base pressure of the preparation chamber was  $10^{-9}$  mbar and the pressure upon  $\text{Co(TCNE)}_x$  preparation was  $\sim 5 \times 10^{-8}$  mbar. Studies were performed *in situ* using photoelectron spectroscopy (PES), near edge X-ray absorption fine structure (NEXAFS) and resonant photoelectron spectroscopy (RPES) at beamline D1011 of the MAX-II storage ring at the synchrotron radiation facility MAX-lab in Lund, Sweden. The (front) end-station is equipped with a Scienta SES electron analyzer and has a custom-built micro-channel plate (MCP) detector for electron yield measurements (NEXAFS). An incident angle  $\theta = 45^\circ$  of the photon beam relative to the sample normal

was used for all types of measurements. The backgrounds are not removed from the NEXAFS or the RPES spectra, neither the second order light nor the spectator decay contributions to the RPES spectra (but those contributions are indicated in the spectra).

Additional PES measurements were performed in our home laboratory by a Scienta<sup>®</sup> ESCA 200 spectrometer. X-ray photoelectron spectroscopy was performed using monochromatized  $\text{Al(K}\alpha)$  X-rays at  $h\nu = 1486.6$  eV. The base pressure of the system was in the  $10^{-9}$  mbar range. The  $\text{Co(TCNE)}_x$  thin films were prepared under the same conditions in the home laboratory as in MAX-lab.

## 3. Results and discussion

The stoichiometry of  $\text{Co(TCNE)}_x$  was estimated from the XPS wide scan, using atomic sensitivity factors which suggested about two TCNE molecules per cobalt ion. Upon PES, NEXAFS and RPES, no oxygen was present (to the detection limit of the measurements), confirming oxygen-free  $\text{Co(TCNE)}_x$ . The C(1s) core level of  $\text{Co(TCNE)}_x$  and  $\text{V(TCNE)}_x$ , respectively, see Fig. 1a, are located at roughly the same position (286.0 and 286.2 eV, respectively). The C(1s) peak of  $\text{V(TCNE)}_x$  has a shake-up feature at the higher binding energy side of the main peak, which is absent for  $\text{Co(TCNE)}_x$  (as well as for  $\text{Fe(TCNE)}_x$  [16]). This indicates that the LUMO of  $\text{Co(TCNE)}_x$  (and  $\text{Fe(TCNE)}_x$ ) is modified as compared to the  $\text{V(TCNE)}_x$  counterpart, which suggests the HOMO to be modified as well. There is an asymmetry at the low binding energy side of C(1s) of  $\text{Co(TCNE)}_x$  which also is present for C(1s) of  $\text{Fe(TCNE)}_x$  [16]. This low-binding energy feature of C(1s) has been seen in low-quality  $\text{V(TCNE)}_x$  films, where it is attributed to a bonding defect: vanadium bonding to vinyl sites of TCNE instead of the cyano ligands [15]. Hence the presence of the C(1s) low-binding energy feature suggests a more disordered film growth for  $\text{Co(TCNE)}_x$  (and for  $\text{Fe(TCNE)}_x$  [16]) as compared to  $\text{V(TCNE)}_x$ .

The N(1s) core level of  $\text{Co(TCNE)}_x$  and  $\text{V(TCNE)}_x$ , see Fig. 1b, are located at the same position, i.e. at 398.8 eV. As for C(1s), N(1s) of  $\text{Co(TCNE)}_x$  (and of  $\text{Fe(TCNE)}_x$  [16]) lacks the shake-up feature, an indication of modified LUMO and HOMO as compared to  $\text{V(TCNE)}_x$ . However, the most striking difference between N(1s) of  $\text{Co(TCNE)}_x$  and  $\text{V(TCNE)}_x$  is that N(1s) of  $\text{V(TCNE)}_x$  is much broader than N(1s) of  $\text{Co(TCNE)}_x$ . We speculate that this is due to that cobalt preferentially bonds to the vinyl groups of TCNE instead of the cyano groups (as in  $\text{V(TCNE)}_x$ ), since C(1s), but not N(1s) is broadened as compared to pristine TCNE. Given that the C(1s) and N(1s) of  $\text{Co(TCNE)}_x$  (and of  $\text{Fe(TCNE)}_x$  [16]) are very different as compared to the corresponding C(1s) and N(1s) core level peaks of  $\text{V(TCNE)}_x$  [5], it indicates the physical and chemical environment to be different in the three compounds.

Download English Version:

<https://daneshyari.com/en/article/7874356>

Download Persian Version:

<https://daneshyari.com/article/7874356>

[Daneshyari.com](https://daneshyari.com)