

# **ABSTRACT BOOK**





BRAZILIAN GOVERNMENT

# **CAMPUS MAP**





















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## Introduction

We have the pleasure to welcome you to the Workshop on Advanced Nanomagnetism Characterization, held during August 30<sup>th</sup> and 31<sup>st</sup>, 2018, at the Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Center for Research in Energy and Materials (CNPEM), Campinas, Brazil. This event is a satellite event of the 16<sup>th</sup> International Conference on Molecule-Based Magnets which will take place at the city of Rio de Janeiro from September 1<sup>st</sup> to 5<sup>th</sup>.

With the development of very sophisticated growth techniques, which allow control of the morphological properties with nanometer resolution, the scientific community produced new materials and heterostructures, where the reduced physical size plays an important role on their properties. On the other hand, the characterization of such nanometric systems is very challenging, and quite often one needs to rely on several complementary techniques to obtain a picture of the properties and characteristics of such samples.

The aim of the workshop is to gather together specialists on diverse techniques used to study magnetism at the nanoscale. We hope this will allow every one of us to get acquainted with some characterization approaches that normally are not within our technique portfolio.

This event would not be possible without the funding from the scientific Brazilian agencies CAPES and CNPq, the kind sponsorship from SPECS GmbH, and the invaluable support from several people inside the CNPEM.

On the behalf of the organizing committee, we hope that at the end of this day and a half meeting, we all can gain new insights on how to tackle the difficult, but very exciting task of understanding and controlling magnetism at the nanoscale.

**Júlio Criginski Cezar** Workshop Coordinator

# **About CNPEM and LNLS**

#### **CNPEM**

The Brazilian Center for Research in Energy and Materials (CNPEM) is a private nonprofit organization located in Campinas, Brazil, which is funded by the Ministry of Science, Technology, Innovation & Communication (MCTIC). It is dedicated to cuttingedge research in materials, nanosciences, life sciences, physics, and chemistry through four National Laboratories: Synchrotron (LNLS), Biosciences (LNBio), Bioethanol (CTBE) and Nanotechnology (LNNano). The four laboratories are open facilities for external users and companies, from Brazil and abroad. They also have teams of researchers to provide support for projects, as well as to conduct joint research programs in biomass, green chemistry, drugs and cosmetics development, characterization of advanced materials, catalysts, etc.

#### LNLS

The Brazilian Synchrotron Light Laboratory (LNLS), located in Campinas, at São Paulo state, operates the only synchrotron light source in Latin America, providing high brilliant light from infrared to X-rays for the analysis of organic and inorganic materials. Designed and built with Brazilian technology, LNLS was inaugurated in 1997 as an open facility to the scientific and industrial communities across the country and abroad.

LNLS is currently engaged in the development and construction of Sirius, the next Brazilian synchrotron light source. It is planned to be a state of the art fourth generation machine, designed to be one of the most advanced in the world. Its ultra-low emittance and thus high brightness will open up new perspectives for research in many fields such as material science, structural biology, nanoscience, physics, earth and environmental science, cultural heritage, among many others.

# **Organizing Committee**

#### **Scientific Committee**

Júlio Criginski Cezar (LNLS – CNPEM) Benjamin Rache Salles (Universidade Federal do Rio de Janeiro) Maria das Graças Fialho Vaz (Universidade Federal Fluminense)

#### Local Committee

Dora Maria Marques (CNPEM) Graziela Pereira Esteves (LNLS – CNPEM) Júlio Carvalho (LNLS – CNPEM) Lucas Dias (CNPEM) Luciana Noronha (LNLS – CNPEM) Murilo Oliveira (CNPEM) Priscila Cassiano Alves (LNLS – CNPEM) Renan Picoreti (LNLS – CNPEM)



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# Program

	Thursday, August 30 <sup>th</sup> , 2018	Friday, August 31 <sup>st</sup> , 2018
8:30h	Registration	
8:50h	Welcome	
9:00h	Matteo Mannini - University of Firenze (invited) X-rays for the characterization of magnetic molecules at the nanoscale	Jan Dreiser - Paul Scherrer Institut (invited) Shedding light on functional molecular magnetic interfaces
10:00h	Daniel E. Bürgler - Forschungszentrum Jülich Spin-Polarized Scanning Tunneling Microscopy and Spectroscopy of Single Hybrid Molecular Magnets	Sadaf Fatima - University of Karachi Atomic scale evidence of the switching mechanism in a photomagnetic CoFe dinuclear Prussian Blue Analogue
10:30h	Coffee break	Coffee break
11:00h	Floriana Tuna - University of Manchester (invited) Molecular Nanomagnets as Electron Spin Qubits: Magnetic, CASSCF and Pulsed EPR Studies	Emilia Annese - Federal University of Rio de Janeiro (invited) In-situ versus ex-situ characterization of hybrid organic-inorganic interface
12:00h	Maximiliano D. Martins - Centro de Desenvolvimento da Tecnologia Nuclear Non-collinear magnetism in Co monolayer on Ru (0001)	Jeovani Brandão - Brazilian Synchrotron Light Laboratory/CNPEM Understanding the formation of nanomagnetic textures imaged by magnetic force microscopy
12:30h	Dayane Souza Chaves - Institut Néel Grenoble Room-temperature chiral magnetic skyrmions in magnetic nanostructures observed by Photoemission Electron Microscope (PEEM )	Lunch / departure to airport
13:00h	Lunch	
14:00h	Stephen Hill - Florida State University (invited) Molecular Nanomagnetism Studies Using High-Field Electron Paramagnetic Resonance	
15:00h	Georgios Velkos - Leibniz-Institut für Festkörper- und Werkstoffforschung Surface magnetism of single molecule magnets based on endohedral metallofullerenes	
15:30h	About the SIRIUS project	
16:00h	Coffee break / Poster Session / Visit to SIRIUS	
18:00h	End of First Day	



# **SPEAKERS PRESENTATIONS**



# Molecular Nanomagnets as Electron Spin Qubits: Magnetic, CASSCF and Pulsed EPR Studies

Dr. Floriana Tuna

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Pulsed-EPR techniques have become increasingly popular in the field of molecular magnetism, being used for both characterization and manipulation of quantum states [1]. Such spin-echo methods provide a means to measure quantum coherence and entanglement in magnetic systems, as well as electron-electron and electron-nuclei interactions [2-4].

This lecture will focus on magnetic and EPR studies of d- and f-block organometallic systems. The compounds show single-ion magnet behaviour, as well as quantum coherence properties, which make them suitable as quantum memories or quantum bits (qubits). The latter are the building blocks of a quantum computer, expected to do calculations that are not possible with our conventional computers. In order to make advances in this field of research, a better understanding of the quantum coherence and its manifestation in molecular systems is necessary.

We characterise our systems through various techniques, including SQUID magnetometry and advanced EPR spectroscopy such as: HYSCORE, ENDOR, ESEEM, which allow investigating the interplay between different relaxation mechanisms in SMMs, as well as testing quantum protocols. We used CASSCF ab-initio calculations to characterise the compounds, and to guide our design of better lanthanide and actinide single-ion magnets, exhibiting larger energy barriers and/or magnetic blocking.

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[7] S.G. McAdams, E.A. Lewis, et al, P. O'Brien, F. Tuna, "Dual functionalization of liquid-exfoliated semiconducting 2H-MoS2 with lanthanide complexes bearing magnetic and luminescence proprieties", Adv. Funct. Mater. 2017, 1703646.

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## Shedding light on functional molecular magnetic interfaces

#### Dr. Jan Dreiser

Swiss Light Source, Paul Scherrer Institut, WSLA/106, CH-5232 Villiguen PSI, Switzerland.

Functional molecular materials such as single-molecule magnets [1], spin-crossover [2] or photomagnetic complexes [3] are attracting a lot of interest because of their potential for applications in the fields of molecular electronics and spintronics. However, in order to construct devices from them, the molecules have to be removed from their native environment and deposited as thin films or submonolayers on suitable substrates. Importantly, the properties of the molecules at such interfaces can differ greatly from the bulk molecular properties because of strong molecule-surface interactions and modified intermolecular interactions [4,5]. In many cases, these interactions have a detrimental effect, removing or weakening the desired molecular properties. Thus, in order to exploit the promising features of the molecules, a good understanding of the molecule-substrate interface is required.

In my talk I will present our recent efforts to understand and control the magnetic properties [6], the organization [7] and other properties of the adsorbed functional molecular complexes. In particular, I will highlight the exceptional properties of terbium and dysprosium double-decker molecules adsorbed on magnesium oxide thin films and report on recent experiments using ferroelectric surfaces.

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### X-rays for the characterization of magnetic molecules at the nanoscale

#### Dr. Matteo Mannini

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Due to the wealth and the tuneability of their properties, molecular materials stand out as a possible answer to the needs for innovative technologies. The ensemble of magnetic molecules constitutes a rich playground for chemists and physicists toward the development of novel molecular based devices also because of this possibility to finely tune the device properties through proper design of the molecular structure and the assembling of established building blocks following a rational design. This idea explains the huge efforts of molecular magnetism [1] community in the exploration of the use of magnetic molecules for the development of novel devices for the information and computation technologies including spintronics and quantum computation. However, a migration from classical materials to future molecular-based devices requires a careful evaluation of the chemical and physical properties of those fragile magnetic systems after that nanostructuration processes have been attempted. Large scale facility-based techniques become fundamental for the verification that their electronic and magnetic features survives to the extreme conditions occurring in single-molecule-device-like environments. Going beyond a morphological characterization allowing to "see" isolated molecular objects, intactness of molecules can be evaluated by using surface sensitive techniques that provide a complete overview of the chemical and electronic properties of those systems. X-ray circular magnetic dichroism (XMCD) experiments (eventually coupled with other techniques) lead to fundamental steps forward in this demanding exploration by directly accessing to static and dynamic magnetic properties of those systems down to the nanoscale. Here we will present our most recent results achieved at the nanoscale on single molecule magnets (SMMs), a peculiar family of molecules showing slow relaxation of the magnetization and peculiar quantum-based effects [1]. SMMs can be assembled on surfaces by adopting wet-chemistry approaches or sublimating them using high vacuum compatible techniques [2] and the combination of several characterization tools allows to demonstrate that their magnetic behaviour can be maintained, lost or enhanced by the interaction with surfaces [3-9].

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## Molecular Nanomagnetism Studies Using High-Field Electron Paramagnetic Resonance

Dr. Stephen Hill

Department of Physics and National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL32310, United States.

Most Electron Paramagnetic Resonance (EPR) research is performed at the X-Band frequency of 9.7 GHz (0.25 Tesla for a free electron). Specialized commercial instruments exist at K- (25 GHz), Q- (35 GHz) and W-Band (95 GHz), operating to magnetic fields up to 6 T. The EPR facilities at the National High Magnetic Field Laboratory (MagLab) in Florida, offer scientists from all over the world opportunities to use several home-built, high-field/high-frequency EPR instruments with continuous coverage from ~10 GHz to >1 THz [1]. Magnets are also available providing magnetic fields up to 45 T — roughly one million times the earth's magnetic field. EPR performed at these extremes offers tremendous advantages for problems spanning diverse research fields from condensed matter physics, to chemistry, to biology. After an overview of the MagLab EPR facility, the remainder of the talk will focus on molecular nanomagnets 3/4 molecules that contain either a single magnetic ion, or multiple exchange-coupled ions that possess a well-defined collective magnetic moment (or spin). These molecules are of interest in terms of their potential use as memory elements in both classical and quantum information processing devices [1,2]. Results obtained from EPR will be highlighted, emphasizing discoveries that have contributed to a shift away from the study of large clusters to simpler molecules containing highly anisotropic magnetic ions such as lanthanides [2] or transition metals with unquenched orbital moments [3-5]. In particular, certain transition metals residing in high-symmetry coordination environments can experience orbitally degenerate ground states and very strong first-order spin-orbit coupling. The resulting giant magnetic anisotropies associated with such species have been measured using very high-field (up to 35 T) EPR [3-5]. If time allows, recent work involving the application of unique pulsed high-field EPR to the study of molecular nanomagnetism will be highlighted [6].

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- [5] Suturina, Zadrozny, Hill, Schnegg, Long, Neese et al., Inorg. Chem. 56, 3102–3118 (2017).
- [6] Greer, Thomas, Hill et al., Inorg. Chem. (submitted).



# **ORAL PRESENTATIONS**



# Understanding the formation of nanomagnetic textures imaged by magnetic force microscopy

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Magnetic textures observed in thin films are the most recent candidates as information carriers to develop the next generation of spintronic devices. To accelerate the process towards the realization of magnetic domain devices, such as magnetic sensors, racetrack memories and domain wall logic, an enhanced control on the formation, stability and motion of the magnetic structures is desired. These textures include worm like domain pattern, magnetic bubbles and the modern skyrmions. In this talk, I present the formation of different nanomagnetic domains configurations in un-patterned thin film multilayers imaged by magnetic force microscopy (MFM). The results show clearly transitions from magnetic field. This behavior sheds light on the skyrmions generation that usually require an external force for their stabilization. Also, the role of different physical properties on the magnetic domains pattern formation and size is determined by means of micromagnetic simulations

# Spin-Polarized Scanning Tunneling Microscopy and Spectroscopy of Single Hybrid Molecular Magnets

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 <sup>3</sup>Jülich-Aachen Research Alliance, Fundamentals of Future Information Technology (JARA-FIT), Forschungszentrum Jülich, Germany

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We discuss the nanomagnetic characterization of individual hybrid molecular magnets by exploiting the topographic, electronic, and magnetic imaging and measuring capabilities of low-temperature spin-polarized scanning tunneling microscopy and spectroscopy (SP-STM/STS) [1]. Hybrid molecular magnets are formed upon chemisorbing aromatic molecules on ferromagnetic transition-metal surfaces. The hybridization between the molecular  $\pi$ -orbitals and the spin-split d-states of the substrate results in a spin-imbalanced molecular density of states (DOS). As a consequence, the chemisorbed molecule exhibits, depending on the molecule-substrate interaction strength, an induced magnetic moment and spin polarization (SP) near the Fermi level or a spin-dependent HOMO-LUMO gap [2,3]. The substrate atoms that are bound to the molecule are also electronically and magnetically modified. Their mutual in-plane exchange coupling is enhanced, whereas the exchange coupling to the surrounding bare substrate atoms in the uppermost layer and to those in the second uppermost layer is reduced. Therefore, the chemisorbed molecule together with the substrate atoms bound to it can be considered as a new magnetic unit, a so-called hybrid molecular magnet, with enhanced coercivity and Curie temperature [4]. In order to study the nanomagnetic properties of such single-molecule hybrids, we deposit in ultrahigh vacuum sub-monolayer amounts of suitable aromatic molecules by sublimation onto pre-cleaned, single-crystalline transition-metal surfaces. STM topography images yield detailed information about the integrity of the molecule after adsorption, the adsorption geometry with respect to the substrate lattice, and also intramolecular orbital resolution on the sub-nm scale. This structural information is required for setting up an atomistic model as input for spin-resolved density-functional theory (DFT) calculations. STS measurements (recording tunneling current I while sweeping the bias voltage V for vertically and laterally fixed tip position) yield conductivity (dI/dV) curves that represent to a good approximation the local DOS of the sample. Conductivity maps measured at a fixed bias voltage V0 while scanning the tip show laterally resolved intensity variations of DOS features at the energy EFermi + Vo, thereby enabling the imaging of molecular orbitals with intramolecular resolution. Using spin-polarized (e.g. ferromagnetic) tips adds magnetic sensitivity due to the magnetoresistance effect between tip and sample. Differences between topography or conductivity data obtained

for parallel and antiparallel alignment of tip and sample magnetizations can be related to the local SP of the sample, thereby enabling the measurement of spatially and energetically resolved SP maps on the sub-nm scale. We present exemplary data for triphenyl-triazine (TPT) molecules adsorbed on 2 ML Fe/W(110) and Co bilayer nanoislands on Cu(111). On both substrates, TPT adsorbs in a well-defined flat geometry such that hybrid molecular magnets are formed. As expected from DFT [5], the hybridization-induced SP on TPT is opposite to that of the Fe or Co substrate. Interestingly, the SP maps reveal in both cases intramolecular variations of the SP among the three phenyl-groups of TPT. On the Fe surface, atomic-scale STM images unveil a highly asymmetric chiral adsorption geometry of the 3-fold symmetric TPT on the 2-fold symmetric substrate. The resulting different bonding and hybridization conditions for each phenyl-group yield different electronic and magnetic properties for each of them [6]. In contrast, the adsorption geometry of TPT on Co(111) is fully symmetric, and we relate the SP variations to the spin-dependent quantum interference pattern of the Co(111) surface state [7]. These examples showcase the power of SP-STM/STS for the detailed characterization of nanoscale magnetic structures, for which geometric, electronic and magnetic structure are highly interlinked.

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# Room-temperature chiral magnetic skyrmions in magnetic nanostructures observed by Photoemission Electron Microscope (PEEM)

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Magnetic skyrmions are chiral spin structures with a whirling configuration. Their topological properties, nanometer size and the fact that they can be moved by small current densities have opened a new paradigm for the manipulation of magnetization at the nanoscale. Chiral skyrmion structures have so far been experimentally demonstrated only in bulk materials and in epitaxial ultrathin films, and under an external magnetic field or at low temperature. We report on the observation of stable skyrmions in sputtered ultrathin Pt/Co/MgO nanostructures at room temperature and zero external magnetic field. We used photoemission electron microscopy combined with X-ray magnetic circular dichroism (XMCD-PEEM) to demonstrate their chiral Néel internal structure which we explain as due to the large strength of the Dzyaloshinskii -Moriya interaction as revealed by spin wave spectroscopy measurements. Our results are substantiated by micromagnetic simulations and numerical models, which allow the identification of the physical mechanisms governing the size and stability of the skyrmions.

## Atomic scale evidence of the switching mechanism in a photomagnetic CoFe dinuclear Prussian Blue Analogue

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Nanoscale magnetic materials are potential candidates for energy efficient, photoswitchable molecule-based information storage. Molecular complexes exhibiting externally-controlled bistable physical properties are well-suited for these applications. The family of Prussian Blue and its analogues, referred as Prussian Blue analogues (PBA), exhibit thermal and photomagnetic bistability [1]. Recently, a dinuclear molecule has been synthesized [2]. It is built from Fe(III) cyanides and Co(II) ions and can be seen as the elementary motif of the Co-Fe Prussian Blue Analogues (PBA). This is the first dinuclear complex to exhibit thermal and photomagnetic bistablility in solid state. The current challenge of designing systems for information storage requires the deep understanding of the thermally and light-induced electron transfer phenomenon and its driving mechanism. Therefore, advanced characterization techniques like X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) are the excellent tools to probe the change in the macroscopic magnetic properties of PBAs and can give local information about the metal centers existing in the structure. In this talk, we present XAS/XMCD results obtained on this molecule as well as on Fe and Co precursors that are its building blocks. Element specific XAS and XMCD measurements at Fe and Co L2,3 edges were performed on the DEIMOS beamline (SOLEIL, France). XMCD at Fe and Co L2,3 edges was measured as a function of temperature ranging from 300K to 4K to follow the thermally induced charge transfer between Fe(III)-Co(II) paramagnetic pair and Fe(II)-Co(III) diamagnetic pair. At 4K, the sample is irradiated by a 660 nm laser that switched the diamagnetic Fe(II)-Co(III) pair to the Fe(III)-Co(II) paramagnetic one. We also followed the relaxation of the photoinduced metastable state as a function of temperature and determined the fraction of paramagnetic Fe(II) low spin and Co(III) high spin species. Another important aspect is to check for the reversibility of the charge-transfer that has been measured by warming the sample to 300 K. In order to achieve detailed interpretation of data and to

extract quantitative information XAS and XMCD spectra were modeled using the Ligand Field Mutiplet theory (LFM) [3]. Through experimental and theoretical approaches combining element selective probes, XAS/XMCD and Ligand Field Multiplet calculations, we were able to evidence the changes occurring at the atomic scale in the electronic and magnetic properties.

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### Non-collinear magnetism in Co monolayer on Ru(0001)

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The combination of the high spatial resolution capability of the scanning tunneling microscopy (STM) with the sensitivity to the spin of the tunneling electrons has been applied to study the magnetic properties of nanomaterials down to the atomic scale [1, 2]. Magnetism in low-dimensionality materials often exhibit different properties in relation to their microscopic counterparts. In some of these nanomaterials such as ultrathin films, the symmetry breaking induced by the interfaces combined with a nonzero spin-orbit coupling may result in the emergence of an additional interaction, the Dzyaloshinskii-Moriya interaction (DMI) [3]. In magnetic systems, DMI can leads to noncollinear magnetic order, such as spin spiral and skyrmions. However, the noncollinear magnetic order mostly result from the competition of DMI with exchange interaction and magnetic anisotropy energy (MAE), which favors collinear states. Here, we present the results of a detailed characterization of the epitaxial growth and the magnetism of ultrathin nanostructures of cobalt on Ru(0001), by using scanning tunneling microscopy (STM) and spectroscopy (STS) [4]. The results reveal the occurrence of noncollinear magnetism driven by Dzyaloshinskii-Moriya exchange in a monolayer (ML) of Co epitaxially grown on Ru(0001). It is shown that the magnetic ground state of the system is a spin spiral state, which evolves to isolated skyrmions by applying external magnetic fields as low as 100 mT. Even though SOI is weak in Ru, a 4d metal, a homochiral spin spiral ground state and isolated skyrmions could be stabilized in Co/Ru(0001). In this case, the absence of magnetocrystalline anisotropy is the essential factor, which enables noncollinear states to evolve in spite of weak SOI. We acknowledge the support from Brazilian agencies CAPES, CNPq, CNEN and FAPEMIG.

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# Surface magnetism of single molecule magnets based on endohedral metallofullerenes

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The contact with conducting substrates results in a substantial deterioration of the magnetic properties of single molecule magnets (SMMs). In particular, interaction with conducting electrons dramatically increases the magnetic relaxation rates, and limits the temperature range, in which magnetic bistability can be observed. Preventing the direct contact of the magnetic species with the substrate via insulator layer have been found to be a viable strategy to overcome this problem.1 Endohedral metallofullerenes (EMFs) provide a possibility to solve this problem without the use of insulator layers.2 The carbon cage itself acts as a protective layer preserving the direct contact of endohedral magnetic species with metals. EMF-based SMMs have been found to show high blocking temperatures and relaxation barriers.3 Furthermore, fullerenes are thermally stable and can be sublimed and deposited on different substrates without the loss of the structural integrity. On the other hand, fullerene cages exhibit rich reactivity, especially in the cycloaddition reactions. This enables exohedral functionalization of EMFs with surface-anchoring groups. These properties enable formation of physi- or chemisorbed monolayers of SMM-EMFs on metallic substrates. The carbon cage shields the endohedral magnetic species from the environment and preserves magnetic bistability and magnetic hysteresis in Dy-EMFs even in contact with metals. In this contribution we will discuss the structural ordering and magnetic properties of such monolayers as studied by X-ray absorption spectroscopy and X-ray magnetic circular dichroism.

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# **POSTER PRESENTATIONS**



#### Study of soft/hard magnetic CoFe2/CoFe2O4 nanocomposite

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The magnetic ferrite like M2+Fe23+O4 (M = Ni; Co, Fe, Li, Mn, Zn, etc.) are used in several applications such as high density magnetic storage [1], electronic devices, biomedical applications [2,3], permanent magnets [4] and hydrogen production [5]. Among the hard ferrites the CoFe2O4 (cobalt ferrite) plays an important role. This material presents some promising characteristics to several technological applications such as high magnet-elastic effect, chemical stability, electrical insulation, moderate saturation magnetization (MS), tunable coercivity (HC) [6,8] and thermal chemical reduction [5,7]. These characteristics allow the cobalt ferrite to be used in several applications. Particularly to permanent magnet applications the parameters MS and HC are of fundamental importance. Both parameters define the quantity (BH)max (figure of merit for permanent magnets) that gives an estimative of the amount of energy that can be stored in a material. The tunable coercivity of cobalt ferrite allows the increase the HC [6]. Furthermore, the thermal chemical reduction enable us to increase the MS through the partial conversion of hard ferrimagnetic compound CoFe2O4 into the soft ferromagnetic iron cobalt (CoFe2), producing the

CoFe2O4(core)/CoFe2(shell) nanocomposite [7]. Moreover, the material CoFe2 can be oxidized and turn again CoFe2O4. The redox effect to CoFe2O4 makes possible the produce hydrogen [5]. In this work we will study magnetic systems where occurs the Exchange Spring effect. This magnetic system is a nanocomposite of Iron Cobalt (CoFe2) and Cobalt Ferrite (CoFe2O4). The prepared nanocomposite is the CoFe2/CoFe2O4 core-shell structured, where the core of the bulk is composed of Iron Cobalt and the Shell is Cobalt Ferrite as made by Zhang et.al. [9]. The CoFe2O4 represents a hard magnetic composite and the CoFe2 is a soft magnetic composite. This study aims a better knowledge of the nanocomposite parts structural parameters influence on the Exchange Spring effect in a way to maximize the maximum energetic product. The precursor material (CoFe2O4) have been prepared by the stoichiometric combustion method [8]. The Iron Cobalt samples have been prepared from the precursor material Cobalt Ferrite total reduction [5]. To obtain the CoFe2 we used a tubular furnace at 350°C with hydrogen atmosphere. The following process occurs: CoFe2O4+4H2CoFe2 + 4H2O(1) To obtain the CoFe2O4 we used tubular furnace with oxygen atmosphere at 380°C where CoFe2 turn cobalt ferrite according the following equation: CoFe2+2O2 CoFe2O4 (2) Both process, reduction (eq. 1) and oxidation (eq. 2) involves change of mass, thence the first measurement was the mass lost in case of reduction or gain in the case of oxidizing. These mass measurements indicate the quantity of each compound in the nanocomposite, defining a production process in which we can control the thickness of the external material (the hard magnetic Cobalt Ferrite). After, the prepared nanocomposites C1, C2 and C3 samples and a pure CoFe2O4 sample were mechanically treated in a balls mill for 1,5h with

6mm diameter zirconia balls, aiming the increase of nanocomposite's coercivity values, previously obtained [6]. The samples were structurally characterized with X-Ray Diffractometer (XRD) and Mossbauer Spectroscopy; the magnetic measurements were made by Vibrant Sample Magnetometer (VSM) analysis. The results showed the formation of the nanocomposite CoFe2/CoFe2O4 in different quantities of Iron Cobalt and Cobalt Ferrite. With the VSM results, we verify the occurrence of Exchange Spring effect in all measured samples. Also, the results showed that the milling process doesn't made any effect on the nanocomposite CoFe2/CoFe2O4 sample's coercivity values, indicating a unknown difference between the synthesized Cobalt Ferrite and the obtained from oxidation process. Exception was observed on pure CoFe2O4 sample, in which the enhanced coercivity is well noted and significant.

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## Magnetic textures in Co/Pd samples

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Magnetic textures such as skyrmions and chiral domains walls have attractive great attention due their properties and technological applications. One path to reach such applications, can be acquired adjusting the physical parameters at the interfaces of multilayered thin films and hence determing the domains type, chirality and size. In this work, we studied the evolution of the anisotropy, magnetization saturation and domains pattern in Co/Pd multilayers by adding an ultrathin Tungsten W layer at the interfaces. These magnetic features were acquired by means of magnetization loops and the domains pattern imaged by magnetic force microscopy (MFM). The out-of-plane remanence drops with the addition of W at the top interfaces, but turns out to increase again with the addition of thicker W layers, overcoming the remanence of the reference sample (no W) for the thickest W layers. This behavior relates to the domains size obtained in the MFM images, which the smallest size coincides with the minimum of the remanence. Structural properties at the interfaces were determined as the multilayer evolves from rougher to flatter interfaces when a continuos W layer is formed. Also, micromagnetic simulations were perfored to elucidate the mechanisms that determine the domain textures and size.

# Magnetic and morphological characterization of electrodeposited cobalt onto CVD graphene

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Graphene, a single layer of graphite, is currently the subject of a masive research interest due to its excellent physical and chemical properties [1]. In the other hand, nanostructured Co materials possess pronounced magnetic characteristics such as superparamagnetism, giant magnetoresistance effect, strong anisotropy, high coercivity, and high-density recording, which of significant importance in diverse technological applications [2,3]. Thus, study graphene-metal properties is crucially important for the development of Co/graphene-based devices. In this work, cobalt was electrodeposited onto CVD Graphene/Cu substrate, during different time intervals, using an electrolyte solution contained a low concentration of cobalt sulfate. The intention was to investigate the details of the resulting magnetic properties of the Co deposits on graphene. After electrodeposition, magnetic measurements were performed using an Alternating Gradient Force Magnetometer (AGFM). These were followed by morphological analysis of the samples with  $\Delta t DEP 10$ , 20, 30 and 100s by atomic force microscopy (AFM) in the tapping mode, and on a pristine CVD graphene/Cu. The results showed that the Co deposits exhibit antiferromagnetic and ferromagnetic behaviors, depending on the deposition time. The studies revealed that the first cobalt electrodeposits onto CVD graphene/Cu was in the form of oxide nanoparticles (this was confirmed by X-ray photoelectron spectroscopy), with antiferromagnetic behavior. The cobalt oxidation process is apparently due to the graphene surface chemistry. For longer deposition times, cobalt exhibits ferromagnetic behavior. The morphological characterizations, by AFM, indicated that up to 30s electrodeposits cobalt nanoparticles are present, whereas for longer deposition times, cobalt metal deposits take place.

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# Persistent organic radical based on 1,3-diazaphenalenyl derivative stabilized without bulky substituents

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The development of stable organic radicals has been attracted much attention of scientists since its first synthesis by Gomberg more than century ago [1]. Since then, a variety of organic open shell compounds has been synthesized, however phenalenyl (Py) type radicals are considered as one of the most promising systems [2]. Py is the smallest part of the graphene, which was synthesized and characterized recently, but unfortunately it was prone to dimerization affording closed shell molecule as most of the radicals [2]. To prevent the -dimerization bulky substituents have to be introduced, but steric impediment caused by the bulky groups inhibits the exchange interaction between the unpaired electron of neighboring organic radicals that restricts the area of their possible applications. Thus, the search for new Py like structures capable of stabilizing the unpaired electron is of great scientific interest in nowadays. For example, theoretical simulations predicted high stability of 1,3-diazaphenalenyl, the structure quite similar to Py but with two nitrogen atoms at positions 1,3 instead of carbonhydrogens [3]. Recently we reported synthesis of itacoperinone (IP), which is a planar heterocyclic closed-shell molecule based on 1,3-diazaphenalene [4], however its detailed characterization by 1HNMR, EPR and Electrochemistry techniques revealed a presence of unpaired electron in this structure. Such, EPR spectrum showed the presence of delocalized electron with a g value of 2.0027. The cyclic voltammetry of IP in acetonitrile using TBA(PF6) as supporting electrolyte showed two redox potentials, Ecation/radical = -0.92 V and Eradical/anion = -1.42 V (Fc/Fc+), which can be assigned to the HOMO and LUMO of IP respectively. Besides, theoretical calculations were performed and confirmed the possibility of formation of stable radical derived from IP. Therefore, the molecule may be potentially interesting for formation of stable planar organic radicals with potential magnetic properties.

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## XMCD investigation of ultra-thin maghemite

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There is a technological interest in magnetic materials at low dimensionalities due to the anisotropy created by increasing the surface to volume ratio. The physical properties of ultrathin maghemite ( $\gamma$ -Fe2O3) have been poorly investigated due to the difficulty to obtaining an single iron oxide phase [1], despite its importance for understanding of phenomena such as spin polarization and metal-insulator transition. In this study we have prepared iron oxide ultra-thin films on Pd[111] at various thicknesses (5 Å to 28 Å ), with layer by layer Fe deposition and dosing O2 in ultra-high vacuum. In-situ X-ray magnetic circular dichroism (XMCD) in TEY detection mode was the chosen surface technique for the magnetic investigation. By low energy electron diffraction (LEED) we have qualitatively examined the surface structure of iron oxides grown on the [111] direction to correlate with its magnetic response. The X-ray absorption spectroscopy (XAS) at the Fe and O edges as function of film thickness were analysed in order to get information about the evolution of maghemite formation and Fe-O hybridization. To determine the critical thickness of maghemite formation, the population of Fe3+ ions in tetrahedral and octahedral sites has been evaluated. For thicker films a small dichroic signal is measured for the oxygen K edge as compared to the iron L3,2 edges, due to the magnetic moment induced by ferrimagnetic ordering of neighboring Fe3+ ions.

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# Tuning perpendicular magnetic anisotropy in CeO2 and Co/Pt multilayered nanoheterostructures.

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Recently, there has been great interest in magnetic nanostructures with perpendicular magnetic anisotropy (PMA) due to several possible technological applications such as spin-transfer torque devices, high-density recording media, and magnetically controlled transmittance in optical devices. Here, we describe the stabilization of PMA in 20-nmthick ceria (CeO2) films integrated to [Co(0.6 nm)/Pt(0.8 nm)]5 multilayers (Co/Pt-ML). We also demonstrate an enhancement of the originally weak perpendicular component of the magnetic anisotropy in the nanocrystalline cerium oxide films. The room-temperature ferromagnetism of these CeO2 films, with wide energy band-gap and transparency to visible light are promising for possible applications in magneto-optical devices. PMA stabilization has been found to be highly dependent on the thickness of the Pt interlayer spacer between ceria and Co/Pt-ML films. For interlayer thicknesses in the order of 10 nm or thinner, magnetization curves with high squareness (MR close to saturation magnetization MS), and with abrupt magnetization switching were observed across the stacking layers. Magnetic force microscopy measurements revealed the presence of domain structures consisting of non-connected labyrinthine patterns dominated by protruding fingers with a low degree of bubbliness. The fractal dimension of these patterns was also found to be inversely correlated to the Pt interlayer thickness. Considering this correlation and the behavior of magnetic domain edge-fields, a mechanism for the PMA stabilization based on the mapping of Co/Pt-ML domains into the CeO2 films has been proposed.

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# Crystal Field Stark Effects on the Upconversion light emission spectra of NaYF4 Cubic Nanoparticles Doped with Yb3+, Er3+ or Dy3+

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NaYF4 nanoparticles (NPs) form in two structures, cubic and hexagonal, each one presenting a different Crystal Electric Field (CEF) Stark effect, that affects the upconversion (UC) light emission of the NPs when doped with rare earth (RE) elements.[1] Therefore, by the knowledge of the CEF parameters, the wavefuncions and energy levels of the RE J-multiplets, it is expected to be of great help for the improvement of the UC light emission. In this work, doped cubic NaYF4 NP's with Yb3+, Er3+ or Dy3+ were investigated by means of Magnetization, Electron Spin Resonance (ESR) and Optical Spectroscopy techniques. Fittings of the temperature and magnetic field dependence magnetization were performed in order to determine the 4th and 6th order CEF parameters, B4 and B6.[2,3] These parameters were used to write down a total Hamiltonian that allows to determine the CEF Stark splitting for all the energy levels of the RE's 4f unfulfilled shell. Our theoretical simulations of the UC light emission line-width leads to  $470 \pm 20$  K for the transition  $4S3/2 \rightarrow 4I15/2$ , which is comparable to the experimental value of  $\sim 650 \pm 50$  K. The ground state of Yb3+, Er3+ and Dy3+ in these cubic NaYF4 NP's was confirmed by our low temperature ESR experiments. Thereby, in this work we give details of how Stark effects affects the overall energy splitting of the various J-multiplets and may explain the fine structure of the UC light emission in theses cubic NaY1-xRExF4.

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#### **Development of sensitive magnetometers at mK temperatures**

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Molecular magnetism has relied, since its birth, on the availability of magnetization data at mK temperatures. While the micro-SQUID technique has historically been important, other techniques can provide precious information, when exported to pushed environments (e.g. mK temperatures and vector fields, and/or fast field-sweep rates). Cantilever torque magnetometry has been used successfully for these purposes before [1-4], but is only rarely available at mK temperatures and with a full 3D rotation of the magnetic field (which can, for example, correct possible misalignements). Here we present magnetic characterisation of single crystal rare-earth based single-molecule magnets by cantilever torque magnetometry designed to be operated inside a dilution refrigerator, down to 12 mK, combined with a superconducting vector magnet to perform angle-dependent measurements for microcrystals. The deflection of the cantilever is measured through a change in the capacitance as a result of the changing spacing between the capacitor plates, and the possibility of improving the sensitivity via optical interferometry is discussed. Magnetisation hysteresis curves can be obtained relative to any sample orientation. Angle resolved torque measurements reveal the relative angles of the anisotropy axes in the samples, identifying any easy and hard magnetisation axes. Additionally, field resolved torque measurements can identify the breaking field of the sample, which is where the applied field surpasses the strength of the anisotropy. The internal anisotropy parameters can be estimated on the basis of this information. Furthermore, this device offers several unique features: to suit the individual sample, the device can easily be reassembled with cantilevers of different shapes and thicknesses and different spacing between cantilever and underlying capacitor plate. Sample placement and removal is simple and cantilevers can be replaced in case of damage. Furthermore, the design is accessible to implementation of other energy sources, such as optical, enabling the possibility of additional manipulation of the samples. We describe the use of torque magnetometry to investigate the anisotropy of molecular magnets, and provide perspective on how the sensitivity of such detectors can be improved to the extent of single-molecule detection, by the use of graphene. Predictions indicate that suspended graphene can behave as a supercapacitor allowing capacitive detection of extremely small displacements, thus providing a tool for magnetic detection of unprecedented sensitivity. Recent advances in the field of molecular graphene nanoribbons [5] may facilitate the actual realisation of such graphene nanodevices.

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# Anisotropic Magnetoresistance Simulated in Cobalt Nanowires with Grain Structure Distribution

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Anisotropic Magnetoresistance (AMR) is founded in several nanomagnetic systems, such as thin films, nanowires, nanodots, etc. Because of this, when performing electrical measurements in these systems, we always have a signal output with an AMR component. In this scenario, we developed a new tool to calculate the pure AMR response in magnetic nanostructures based on micromagnetic simulations, as follows: (i) first we simulated the magnetic nanostructure, in order to acquire the magnetic texture (mx, my and mz), (ii) we define de ratio of the AMR response (or experimentally measured) and (iii) we solve the electrical problem mixed with the previously acquired magnetic components, which combined will give rise to changes in the material resistivity (AMR-response). As a first result we considered, in Mumax<sup>3</sup>, a thin cobalt nanowire ( $lx = 1 \mu m$ , ly = 100 nm and lz = 35 nm) with a grain size distribution (d =  $4.82\pm1.00$  nm), having, each grain, a uniaxial axis (k =  $45\times104$  J/m<sup>3</sup>) with a random orientation. Then, we applied both: an electrical current (I) along the xdirection and an external magnetic field (H) in the xy-plane forming an angle ( $\theta = 0, 15$ , 20, 30, 45, 60, 80 and 90°) between current and magnetic field. With this approach, we were able to predict the AMR response and index each peak with the correspondent magnetization change. This knowledge, allowed us to, given an AMR measurement, inquire about the magnetization behavior in a sample, providing more information on new magnetic nanostructures investigation.



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