

## DS 2: Towards Molecular Spintronics

Time: Monday 11:45–13:45

Location: H 2013

**Invited Talk** DS 2.1 Mon 11:45 H 2013  
**Tunable electron spin resonance spectroscopy of multi-center paramagnetic molecular complexes in strong magnetic fields**  
 — ●VLADISLAV KATAEV — IFW Dresden, D-01171 Dresden

Determination of the low-energy spectrum of spin states and magnetic anisotropy is an important prerequisite on the route of functionalization of magnetically active molecular complexes for molecular based spintronics. Owing to the increasing complexity of the metal ion polynuclear complexes which combine in a single molecule a large number of interacting transition metal ions, the resulting spin states have a large multiplicity and a complex structure. High magnetic field electron spin resonance (ESR) spectroscopy enables to selectively tune different spin states into the resonance with external microwave radiation and thus to determine the relative energies of the spin levels as well as the magnitude and sign of the magnetic anisotropy. As an example, we will discuss our recent ESR and magnetization measurements of several novel molecular complexes whose magnetic cores are built of interacting paramagnetic  $3d$ -ions, such as, e.g.,  $[L_2Ni_4(N_3)(O_2CAda)_4](ClO_4)$  and  $[(L^2)Ni_2(\mu-pydz)(N_3)_2](BPh_4)_2$ . Experimental data give evidence that the ground state and magnetic anisotropy depend sensitively on the details of the intramolecular bonding geometry and ligand coordination that can be tuned by means of synthetic chemistry. Different spin states can be realized: (i) a nonmagnetic state which can be turned into a magnetic one in strong magnetic fields; (ii) a strongly magnetic ground state with substantial negative magnetic anisotropy, i.e. functionalities constitutive for applications in molecular based spintronics.

**Invited Talk** DS 2.2 Mon 12:15 H 2013  
**Coordinated metal centers: Single-molecule magnets and highspin to lowspin switching**  
 — ●PAUL MÜLLER — Institut für Physik der Kondensierten Materie, Universität Erlangen-Nürnberg

Coordinated metal ions are the essential active centers of many molecules. They are quantum dots with an energy spectrum which can be tuned by the coordinating ligands. Even simple complexes with Mn, Fe, Co, or Cu centers show spectacular physical properties. The structural and electronic properties were studied at the single-molecule level by scanning-tunneling microscopy and current-imaging tunneling spectroscopy (CITS). We applied these methods to several single-molecule magnets and a spin-crossover polymer incorporating supramolecular  $Fe^{II}$  complexes. As the electronic density of states near the Fermi level is dominated by the metal  $3d$  orbitals, CITS spectroscopy can visualize single metal ions in single-molecule magnets, even if these ions are embedded into the sheath of the organic ligand. Therefore, the magnetic state of these ions is accessible to spectroscopy with atomic resolution. CITS measurements of the spin-crossover polymer revealed a high conductivity contrast between monomers in the highspin and in the lowspin state, respectively. Spontaneous switching between these two states was also recorded. This work was done in collaboration with M.S. Alam, V. Dremov, T. Glaser, J. Kortus, Y. Koval, J.-M. Lehn, U. Mitra, A. Postnikov, M. Ruben, R. Saalfrank, M. Stocker, S. Strömsdörfer, and A. Volkov.

**Invited Talk** DS 2.3 Mon 12:45 H 2013  
**Substrate-induced magnetic ordering and switching of iron porphyrin molecules**  
 — ●H. WENDE<sup>1</sup>, M. BERNIEN<sup>2</sup>, J. LUO<sup>2</sup>, C. WEIS<sup>1</sup>, N. PONPANDIAN<sup>2</sup>, J. KURDE<sup>2</sup>, J. MIGUEL<sup>2</sup>, M. PIANTER<sup>2</sup>, X. XU<sup>2</sup>, PH. ECKHOLD<sup>2</sup>, W. KUCH<sup>2</sup>, K. BABERSCHKE<sup>2</sup>, P. SRIVASTAVA<sup>1</sup>, P.M. PANCHMATIA<sup>3</sup>, B. SANYAL<sup>3</sup>, P.M. OPPENEER<sup>3</sup>, and O. ERIKSSON<sup>3</sup> — <sup>1</sup>Universität Duisburg-Essen, Fachbereich Physik — <sup>2</sup>Freie Universität Berlin, Fachbereich Physik — <sup>3</sup>Department of Physics, Uppsala University, Sweden

Paramagnetic porphyrin molecules in contact with a metallic substrate

are promising as building blocks in molecular nano-electronics. For this purpose the manipulation of the spin of the central  $3d$  atom in this biologically significant molecule is essential. Here, we study the structural orientation and the magnetic coupling of *in-situ* sublimated Fe porphyrin molecules on ferromagnetic Ni and Co films which are epitaxially grown on Cu(100). These studies utilize NEXAFS at the C and N K-edges, and XMCD at the Fe, Co and Ni  $L_{2,3}$ -edges, which provide element-specific magnetic properties. In a combined experimental-computational study we demonstrate that due to an indirect, super-exchange interaction between Fe atoms in the molecules and atoms in the substrate (Co or Ni) the paramagnetic molecules can be made to order ferromagnetically. The Fe magnetic moment can be rotated along directions in-plane as well as out-of-plane by a magnetization reversal of the substrate, thereby opening up an avenue for spin-dependent molecular electronics. Supported by BMBF (05KS4KEB5) and DFG (SFB 658, Heisenberg-Programm).

DS 2.4 Mon 13:15 H 2013  
**Controlling the magnetization direction in molecules via oxidation state**  
 — ATODIRESEI NICOLAE<sup>1</sup>, PETER H. DEDERICHS<sup>1</sup>, YURIY MOKROUSOV<sup>2</sup>, LARS BERGQVIST<sup>1</sup>, GUSTAV BIHLMAYER<sup>1</sup>, and ●STEFAN BLÜGEL<sup>1</sup> — <sup>1</sup>Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany — <sup>2</sup>Institute for Applied Physics, University of Hamburg, 20355 Hamburg, Germany

By means of *ab initio* calculations we predict that it is possible to manipulate the magnetization direction in organic magnetic molecules by changing their oxidation state. We demonstrate this novel effect on the  $Eu_2(C_8H_8)_3$  molecule, in which the hybridisation of the outer  $\pi$ -rings states with the Eu  $4f$ -states causes a redistribution of the orbitals around the Fermi level leading to a strong ferromagnetism due to a hole-mediated exchange mechanism. As a key result, we predict an oscillatory behavior of the easy axis of the magnetization as a function of the oxidation state of the molecule - a new effect, which could lead to revolutionary technological applications. Support by the DFG-SPP 1243 is gratefully acknowledged.

DS 2.5 Mon 13:30 H 2013  
**A first-principles DFT study of magnetic properties of a series of complexes based on a hexaaza-dithiophenolate ligand**  
 — ●CLAUDIA LOOSE<sup>1</sup>, ELISEO RUIZ<sup>2</sup>, BERTHOLD KERSTING<sup>3</sup>, and JENS KORTUS<sup>1</sup> — <sup>1</sup>Institut für Theoretische Physik, TU Bergakademie Freiberg, Leipziger Str. 23, D-09599 Freiberg, Germany — <sup>2</sup>Departament de Química Inorgánica and Institut de Recerca de Química Teórica i Computacional, Universitat de Barcelona, Diagonal 647,08028 Barcelona, Spain — <sup>3</sup>Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany

We studied a series of complexes based on a hexaaza-dithiophenolate ligand by first-principles DFT as implemented in the all-electron NRL-MOL code. The main focus of our work was on the effect of different bridges and different metal centers on the magnetic exchange coupling. In agreement with experimental results we predict correctly ferromagnetic or antiferromagnetic coupling depending on bridge or metal center. Only in the case of  $Ni^{2+}$ -ions we find ferromagnetic coupling. The use of other metal centers results in a strong antiferromagnetic coupling.

Interestingly, the ferromagnetic coupling in case of  $Ni^{2+}$  complexes can be tuned by changing the third bridging ligand. Depending on the bridge the magnetic coupling can be changed between strong antiferromagnetic to strong ferromagnetic coupling. This behavior can be understood within the framework of the Hay-Thibeault-Hoffmann model, which relates the energies of the magnetic orbitals to the magnetic exchange coupling.