

## MA 14: Bio- and Molecular Magnetism

Time: Tuesday 9:30–12:15

Location: HSZ 401

MA 14.1 Tue 9:30 HSZ 401

**Magnetic Coupling of Gd<sub>3</sub>N@C<sub>80</sub> Endohedral Fullerenes to a Substrate** — CHRISTIAN F. HERMANN<sup>1</sup>, ●MATTHIAS BERNIEN<sup>1</sup>, ALEX KRÜGER<sup>1</sup>, CHRISTIAN SCHMIDT<sup>1</sup>, SÖREN T. WASSERROTH<sup>1</sup>, GELAVIZH AHMADI<sup>1</sup>, BENJAMIN W. HEINRICH<sup>1</sup>, MARTIN SCHNEIDER<sup>2</sup>, PIET W. BROUWER<sup>2</sup>, KATHARINA J. FRANKE<sup>1</sup>, EUGEN WESCHKE<sup>3</sup>, and WOLFGANG KUCH<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin — <sup>2</sup>Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin — <sup>3</sup>Helmholtz-Zentrum Berlin für Materialien und Energie, Albert-Einstein-Straße 15, 12489 Berlin

Using magnetic endohedral fullerenes for molecular spintronics requires control over their encapsulated magnetic moments. We show by field-dependent x-ray magnetic circular dichroism measurements of Gd<sub>3</sub>N@C<sub>80</sub> endohedral fullerenes adsorbed on a Cu surface that the magnetic moments of the encapsulated Gd atoms lie in a 4f<sup>7</sup> ground state and couple ferromagnetically to each other. When the molecules are in contact with a ferromagnetic Ni substrate, we detect two different Gd species. The more abundant one couples antiferromagnetically to the Ni magnetization, whereas the other one exhibits a stronger and ferromagnetic coupling to the substrate. Both of these couplings to the substrate can be explained by an indirect exchange mechanism mediated by the carbon cage. The origin of the distinctly different behavior may be attributed to different orientations and thus electronic coupling of the carbon cage to the substrate.

Financial support by the DFG (Sfb 658) is gratefully acknowledged.

MA 14.2 Tue 9:45 HSZ 401

**Interaction of FeP and FePc with magnetic surfaces: adsorption structures, magnetic coupling and spin manipulation** — ●BARBARA BRENA<sup>1</sup>, HEIKE HERPER<sup>1</sup>, SUMANTA BHANDARY<sup>1</sup>, DAVID KLAR<sup>2</sup>, HEIKO WENDE<sup>2</sup>, OLLE ERIKSSON<sup>1</sup>, and BIPLAB SANYAL<sup>1</sup> — <sup>1</sup>Department of Physics and Astronomy, Uppsala University, Box 516, 751 20 Uppsala, Sweden — <sup>2</sup>Faculty of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Lotharstraße 1, D-47048 Duisburg, Germany

The interaction of organic molecules like porphyrins and phthalocyanines containing divalent 3d transition metals with magnetic substrates provides a possible mechanism of magnetic switching. We have studied the chemisorption of Fe porphyrins (FeP) and of Fe phthalocyanines (FePc) on Co(001) by means of Density Functional Theory with the GGA+U method, including van der Waals dispersion forces. Two different adsorption mechanisms were identified for the two molecules. In both cases a ferromagnetic coupling with the surface was observed, but while the FePc's maintain a magnetic moment of about 2  $\mu_B$ , close to the gas phase value, the magnetic moment of the FeP's is increased up to about 4  $\mu_B$ . The change to high spin (S=2) in FeP is driven by the stretching of the Fe-N molecular bonds to more than 2.04 Å, due to the strong chemical interaction with the substrate. The same results have been obtained for FeP chemisorbed on Ni(001), Ni(110) and Ni(111). Fe L edge and N K edge experimental absorption spectroscopy results confirm our theoretical findings related to the magnetic coupling and to the adsorption structure of the molecules.

MA 14.3 Tue 10:00 HSZ 401

**FePc on Co(001): Influence of surface oxidation on structure, magnetism, and exchange coupling** — ●HEIKE C. HERPER<sup>1</sup>, BARBARA BRENA<sup>1</sup>, SUMANTA BHANDARY<sup>1</sup>, DAVID KLAR<sup>2</sup>, HEIKO WENDE<sup>2</sup>, BIPLAB SANYAL<sup>1</sup>, and OLLE ERIKSSON<sup>1</sup> — <sup>1</sup>Department of Physics and Astronomy, Uppsala University, Sweden — <sup>2</sup>Fakultät für Physik und CeNIDE, Universität Duisburg-Essen, Germany

We present a density functional theory study combined with x-ray absorption spectroscopy measurements of the electronic and magnetic properties of Fe phthalocyanine (FePc) molecules on fcc Co(001) and c(2×2)O/Co(001). On the bare Co substrate one adsorption site is clearly preferred whereas the oxygen adlayer screens the molecule-substrate interaction and the energy differences between different adsorption sites become smaller. Moreover the coupling between the Fe center and the Co surface switches from ferromagnetic to antiferromagnetic and the coupling strength is reduced due to the O layer. [1] Notably the coupling mechanisms also differ. On the Co(001) substrate a mixture of direct coupling between Fe and Co and an indirect

coupling via the benzene rings is obtained from the DFT calculations whereas on the oxidized surface, an 180° coupling between Fe and Co via O dominates. Despite the changes in adsorption site and coupling, the spin state of the molecule is S = 1 on both substrates.

[1] D. Klar et al., submitted to PRB

MA 14.4 Tue 10:15 HSZ 401

**Magnetization studies of Cu-(bis) oxamato complexes with ferrocenium ligand** — ●AZAR ALIABADI<sup>1</sup>, ANDREAS PETR<sup>1</sup>, MOHAMMAD A. ABDULMALIC<sup>2</sup>, TOBIAS RÜFFER<sup>2</sup>, VLADISLAV KATAEV<sup>1</sup>, and BERND BÜCHNER<sup>1</sup> — <sup>1</sup>IFW Dresden, Dresden, Germany — <sup>2</sup>Institute of Chemistry, Chemnitz University of Technology, Chemnitz, Germany

Magnetic properties of Cu-(bis) oxamato complexes with ferrocenium ligand ([<sup>n</sup>Bu<sub>4</sub>N]<sub>2</sub>[Cu(1,1'-fcb)] (1) and [Cu<sub>3</sub>(1,1'-fcb)(pmdta)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub> (2)) were studied by static magnetic susceptibility and ESR spectroscopy.

For 1 a weak antiferromagnetic coupling between the Cu(II) and Fe(III) ions has been obtained. For 2 an antiferromagnetic coupling of -64 cm<sup>-1</sup> ions and a weak ferromagnetic coupling between the central Cu(II) ion and the Fe(III) ion have been found.

The ESR spectrum of 1 at  $f = 9.56$  GHz and at 4K is a superposition of a signal from Cu(II) and of additional signals which can be attributed to a ferrocenium cation. The shape and the position of the peaks clearly demonstrate two different phases of ferrocenium.

The ESR spectrum of 2 at 4K consists of a single line at a field of 0.32 T which can be assigned to a joint resonance response of three Cu(II) ions and one Fe(III) ion. The calculated isotropic g-factor 2.11 is typical to a g-factor of Cu(II) and also indicates a strong distortion of the axial symmetry in ferrocenium cation.

We discuss possible correlations between the structure of the complexes and their magnetic properties.

MA 14.5 Tue 10:30 HSZ 401

**High-field ESR and magnetization studies of a binuclear Ni(II) complex** — ●AZAR ALIABADI<sup>1</sup>, KAROLINE RÜHLIG<sup>2</sup>, TOBIAS RÜFFER<sup>2</sup>, VLADISLAV KATAEV<sup>1</sup>, HEINRICH LANG<sup>2</sup>, and BERND BÜCHNER<sup>1</sup> — <sup>1</sup>IFW Dresden, Dresden, Germany — <sup>2</sup>Institute of Chemistry, Chemnitz University of Technology, Chemnitz, Germany

We have investigated magnetic properties of a binuclear Ni(II) complex by means of the static magnetization and high-field high-frequency tunable electron spin resonance (HF-ESR). In this compound, two Ni(II) ions each having a spin S=1 are coupled antiferromagnetically which leads to a S<sub>tot</sub> = 0 ground state.

Frequency-dependent HF-ESR spectra yield a g-factor of 2.22. Analysis of the frequency dependence of the ESR signals reveals a positive anisotropy (D > 0) corresponding to an easy plane situation and transverse anisotropy for each Ni ion. The calculation of the magnetic field dependence of the spin state energies from the relevant spin Hamiltonian with the experimentally determined set of parameters predicts a change of the ground state from a nonmagnetic singlet state to magnetic ones with increasing the magnetic field due to the level crossings. Such tuning of the ground state by application of a strong magnetic field has been confirmed in the HF-ESR experiments.

## 15 min. break

MA 14.6 Tue 11:00 HSZ 401

**Magnetization studies of Cu-(bis) oxamato complexes with ferrocenium ligand** — AZAR ALIABADI<sup>1</sup>, ●ANDREAS PETR<sup>1</sup>, MOHAMMAD A. ABDULMALIC<sup>2</sup>, TOBIAS RÜFFER<sup>2</sup>, VLADISLAV KATAEV<sup>1</sup>, and BERND BÜCHNER<sup>1</sup> — <sup>1</sup>IFW Dresden, Dresden, Germany — <sup>2</sup>Institute of Chemistry, Chemnitz University of Technology, Chemnitz, Germany

Magnetic properties of Cu-(bis) oxamato complexes with ferrocenium ligand ([<sup>n</sup>Bu<sub>4</sub>N]<sub>2</sub>[Cu(1,1'-fcb)] (1) and [Cu<sub>3</sub>(1,1'-fcb)(pmdta)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub> (2)) were studied by static magnetic susceptibility and ESR spectroscopy.

For 1 a weak antiferromagnetic coupling between the Cu(II) and Fe(III) ions has been obtained. For 2 an antiferromagnetic coupling of -64 cm<sup>-1</sup> ions and a weak ferromagnetic coupling between the central Cu(II) ion and the Fe(III) ion have been found.

The ESR spectrum of 1 at  $f = 9.56$  GHz and at 4K is a superposition of a signal from Cu(II) and of additional signals which can be

attributed to a ferrocenium cation. The shape and the position of the peaks clearly demonstrate two different phases of ferrocenium.

The ESR spectrum of 2 at 4K consists of a single line at a field of 0.32 T which can be assigned to a joint resonance response of three Cu(II) ions and one Fe(III) ion. The calculated isotropic  $g$ -factor 2.11 is typical to a  $g$ -factor of Cu(II) and also indicates a strong distortion of the axial symmetry in ferrocenium cation.

We discuss possible correlations between the structure of the complexes and their magnetic properties.

MA 14.7 Tue 11:15 HSZ 401

**Effects of the DM-interaction on thermodynamic properties of a small spin system** — ●CHRISTIAN HEESING and JÜRGEN SCHNACK — Universität Bielefeld, Bielefeld, Germany

The magnetism of many magnetic molecules is dominated by isotropic Heisenberg exchange interactions. For 3d elements anisotropic contributions are usually small. Nevertheless, they can have drastic consequences at low temperatures as for instance on bistability and quantum tunnelling in the case of easy-axis anisotropies.

In this contribution we investigate the effect of the Dzyaloshinskii-Moriya (DM) interaction [1,2] on thermodynamic magnetic observables such as the low-temperature magnetization. The full Hamiltonian contains Heisenberg exchange, Zeeman term, and Dzyaloshinskii-Moriya interaction. We investigate as an archetypical model system the cuboctahedron. Thermodynamic observables are systematically compared for various ratios of DM and Heisenberg interaction strength.

[1] T. Moriya, Phys. Rev., 1960, 120, 90-98

[2] I. Dzyaloshinskii, J. Phys. Chem. Solids, 1958, 4, 241-255

MA 14.8 Tue 11:30 HSZ 401

**Magnetization curves of deposited spin clusters** — ●HENNING-TIMM LANGWALD and JÜRGEN SCHNACK — Bielefeld University, Bielefeld, Germany

For future technological applications deposited magnetic clusters offer a significant potential. To utilize this potential requires to characterize these clusters while they are in contact with a substrate. Experimentally, techniques such as spin-flip inelastic tunneling spectroscopy are very useful in this context. These techniques can be used to determine e.g. exchange parameters for effective spin models of the magnetic clusters. One possible approach here is to detect ground state level crossings in an applied magnetic field which serve as fingerprint for the aforementioned spin models.

In this talk we address antiferromagnetic spin chains on a metallic substrate theoretically. The coupling to a conduction electron band of the substrate can lead to a screening of a part of the spin chain and thus

influence the crossing fields. By means of the Numerical Renormalization Group method (NRG) we investigate how the exchange coupling to the substrate's conduction electrons influences the magnetic properties and show the differences between partial and full screening of the spin closest to the substrate.

MA 14.9 Tue 11:45 HSZ 401

**Anisotropic superexchange in  $\text{Mn}_6^{\text{II}}\text{Os}^{\text{III}}$  single-molecule magnets** — ●JÜRGEN SCHNACK — Bielefeld University, P.O. box 100131, D-33501 Bielefeld

Transition metal substitution from 3d to 5d elements may result in strongly anisotropic exchange interactions with a pronounced influence on the anisotropic magnetic response and the behavior as a single-molecule magnet. Here we present recent theoretical investigations of a new compound involving osmium (III).

V. Höke, A. Stammler, H. Bögge, J. Schnack, T. Glaser, Inorg. Chem., in press.

MA 14.10 Tue 12:00 HSZ 401

**A Spin-Crossover Complex on Surfaces** — ●MATTHIAS BERNIEN<sup>1</sup>, THIRUVANCHERIL G. GOPAKUMAR<sup>2</sup>, HOLGER NAGGERT<sup>3</sup>, FRANCESCA MATINO<sup>2</sup>, CHRISTIAN F. HERMANN<sup>1</sup>, ALEXANDER BANNWARTH<sup>3</sup>, SVENJA MÜHLENBEREND<sup>2</sup>, ALEX KRÜGER<sup>1</sup>, DENNIS KRÜGER<sup>1</sup>, FABIAN NICKEL<sup>1</sup>, WALDEMAR WALTER<sup>1</sup>, RICHARD BERNDT<sup>2</sup>, WOLFGANG KUCH<sup>1</sup>, and FELIX TUCZEK<sup>3</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin — <sup>2</sup>Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel — <sup>3</sup>Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, 24098 Kiel

The manipulation of the spin-state of molecules on surfaces is a promising route towards tailor-made molecular building blocks for spintronic devices. Spin crossover (SCO) molecules are appealing since their spin state can be switched by external stimuli, such as temperature and light. Recently, a lot of research has been devoted to vacuum-deposition of SCO molecules using neutral complexes.

We have studied submono-, mono-, and multilayers of the Fe(II) SCO complex  $[\text{Fe}(\text{bpz})_2(\text{phen})]$  (bpz=dihydrobis(pyrazolyl)borate, phen=1,10-phenanthroline) by near-edge x-ray absorption fine structure and scanning tunneling microscopy. We find that  $[\text{Fe}(\text{bpz})_2(\text{phen})]$  in direct contact with a Au(111) surface dissociates into the four-coordinate complexes,  $[\text{Fe}(\text{bpz})_2]$ , and phen molecules. Molecules in the second layer, on the other hand, are intact and show a SCO transition. — Financial support by the DFG (Sfb 658 and 677) is gratefully acknowledged.