

## MA 16: Bio- and Molecular magnetism

Time: Tuesday 9:30–12:30

Location: EB 202

MA 16.1 Tue 9:30 EB 202

**Ferromagnetic Cluster Spin Wave Excitation in the High Spin Molecules  $Mn_{18}Sr$  and  $Mn_{19}$**  — ●SIYAVASH NEKURUH<sup>1</sup>, M. KLINGELE<sup>1</sup>, J. NEHRKORN<sup>1</sup>, K. PRSA<sup>1</sup>, B. BURGER<sup>2</sup>, A.M. AKO<sup>2</sup>, C.E. ANSON<sup>2</sup>, Y. LAN<sup>2</sup>, A.K. POWELL<sup>2</sup>, and O. WALDMANN<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg, Germany — <sup>2</sup>Institut für Anorganische Chemie, Karlsruhe Institut für Technologie (KIT)

The ferromagnetically coupled molecule  $Mn_{19}$  has attracted considerable interest in the past because of its huge high-spin ground state  $S = 83/2$ . From the chemistry point of view determining the exchange coupling constants and their comparison to e.g. ab initio result is of interest, while physically it is highly interesting to understand the spin-wave excitations in such a molecule. The huge Hilbert space and intricate topology of  $Mn_{19}$  complicate the analysis of experimental data enormously, and hence the simpler molecules  $Mn_{10}$  and  $Mn_{18}Sr$ , which can be regarded as model compounds for  $Mn_{19}$ , were studied.

We here present a detailed study of the magnetic excitations in  $Mn_{18}Sr$  and  $Mn_{19}$  by INS. For the determination of the exchange constants of  $Mn_{18}Sr$  we used the positions of two cold peaks in the measured INS spectra and the magnetic susceptibility simultaneously for fitting. In  $Mn_{19}$  one excitation is observed at low energies, which is not present in  $Mn_{10}$  and  $Mn_{18}Sr$  and shows an uncommon temperature dependence. As a result  $Mn_{19}$  cannot be treated by a non-interacting spin-wave picture, but requires an inherent many-body description.

MA 16.2 Tue 9:45 EB 202

**High-field ESR study of a new ferrous cubane SMM** — ●AZAR ALIABADI<sup>1</sup>, FELIX J. KLINKE<sup>2</sup>, SERHIY DEMESHKO<sup>2</sup>, VLADISLAV KATAEV<sup>1</sup>, FRANC MEYER<sup>2</sup>, and BERND BÜCHNER<sup>1</sup> — <sup>1</sup>IFW Dresden, Dresden, Germany — <sup>2</sup>Institute of Inorganic Chemistry, Georg-August-University, Göttingen, Germany

Magnetic properties of a cube-like tetranuclear complex with a  $\{Fe_4O_4\}$  core have been investigated by means of the high-field high-frequency tunable electron spin resonance (HF-ESR). Four Fe(II) spins  $S = 2$  in the complex are coupled ferromagnetically yielding a high-spin ground state with  $S_{total} = 8$ . The ESR spectra consist of a single line in a frequency range  $\leq 332$  GHz, whereas at higher frequencies a low magnetic field line appears at 4 K. The second line at the low magnetic field arises with increasing temperature. A transfer of the spectral weight to higher magnetic field at high temperatures gives evidence for an easy axis magnetic anisotropy for the entire cube. Simulated powder averaged ESR spectra for the case of the collinear alignment of four Fe(II) spins with an easy axis magnetic anisotropy agrees well with the experimental data. The calculated energy levels scheme of this system suggests a spin doublet ground state  $|8, \pm 8\rangle$  which confirms the negative sign of the axial magnetic anisotropy parameter D.

The observation of a high spin ground state with the easy axis magnetic anisotropy for the  $\{Fe_4O_4\}$ -cube suggests a single-molecule magnet (SMM) behavior of the studied complex.

MA 16.3 Tue 10:00 EB 202

**Electron spin density on the N atoms of CuII- bis(oxamidato) complexes: a pulse ELDOR detected NMR study** — ●AZAR ALIABADI<sup>1</sup>, RUSLAN ZARIPOV<sup>2</sup>, MOHAMMAD A. ABDULMALIC<sup>3</sup>, EVGENIYA VAVILOVA<sup>2</sup>, VIOLETA VORONKOVA<sup>2</sup>, TOBIAS RÜFFER<sup>3</sup>, VLADISLAV KATAEV<sup>1</sup>, KEV SALIKOV<sup>2</sup>, and BERND BÜCHNER<sup>1</sup> — <sup>1</sup>IFW Dresden, Dresden, Germany — <sup>2</sup>Zavoisky Physical Technical Institute, RAS, Kazan, Russia — <sup>3</sup>Institute of Chemistry, TU Chemnitz, Chemnitz, Germany

Mononuclear  $Cu(II)$ - bis(oxamidato) complexes are used for the synthesis of their corresponding trinuclear complexes which are excellently suited to study magnetic superexchange phenomena.

To estimate the spin density distribution, which is a measure of the exchange constant, we have determined the hyperfine (HF) tensors for four N atoms of mononuclear  $Cu(II)$ - bis(oxamidato) complexes containing phenylene, ethyl and alkyl nitrogen ligands ( $CuN_2^{aryl}N_2^{ethyl}/CuN_2^{aryl}N_2^{alkyl}$ ) by a pulse ELDOR detected NMR (EDNMR) experiment at 35 GHz and 20 K. We discuss a relationship between the spin density distribution of mononuclear complexes and the magnetic exchange couplings in their corresponding trinuclear complexes.

In particular, the obtained spin densities enable us to explain unexpectedly low J values of trinuclear Cu(II)-bis(oxamidato) complexes ( $J = -[52 - 66]cm^{-1}$ ) compared to the larger value for trinuclear Cu(II)-bis(oxamatato) complex ( $J = -89cm^{-1}$ ).

MA 16.4 Tue 10:15 EB 202

**Quantum signatures of a molecular nanomagnet in direct magnetocaloric measurements** — JOSEPH W. SHARPLES<sup>1</sup>, DAVID COLLISON<sup>1</sup>, ERIC J. L. MCINNES<sup>1</sup>, ELIAS PALACIOS<sup>2</sup>, MARCO EVANGELISTI<sup>2</sup>, and ●JÜRGEN SCHNACK<sup>3</sup> — <sup>1</sup>Chemistry, The University of Manchester, UK — <sup>2</sup>CSIC, Universidad de Zaragoza, Spain — <sup>3</sup>Physics, Bielefeld University, Germany

Geometric spin frustration in low-dimensional materials, such as the two-dimensional kagome or triangular antiferromagnetic nets, can significantly enhance the change of the magnetic entropy and adiabatic temperature following a change in the applied magnetic field, that is, the magnetocaloric effect. In principle, an equivalent outcome should also be observable in certain high-symmetry zero-dimensional, that is, molecular, structures with frustrated topologies. Here we report experimental realization of this in a heptametallic gadolinium molecule. Adiabatic demagnetization experiments reach  $\sim 200$  mK, the first sub-Kelvin cooling with any molecular nanomagnet, and reveal isentropes (the constant entropy paths followed in the temperature-field plane) with a rich structure. The latter is shown to be a direct manifestation of the trigonal antiferromagnetic net structure, allowing study of frustration-enhanced magnetocaloric effects in a finite system.

J.W. Sharples, D. Collison, E.J.L. McInnes, J. Schnack, E. Palacios, M. Evangelisti, Nature Communications 5 (2014) 5321

MA 16.5 Tue 10:30 EB 202

**Magnetic coupling in unligated and ligated FePc sandwiches** — ●HEIKE C. HERPER and BARBARA BRENA — Department of Physics and Astronomy, Uppsala University, Sweden

Molecular magnetic materials are intensively discussed as candidates for future electronic devices however switching the spin state or changing the magnetic coupling is still a challenging task. We have performed an ab initio study of the magnetic and structural properties of sandwiches of FePc molecules which serve as a model system for transition metal based Pc complexes. Investigations include molecules in gas phase as well as adsorbed on a metal substrate. The two FePc molecules are weakly bonded and the calculated exchange coupling is smaller than 20 meV such that a flipping from ferromagnetic (FM) to antiferromagnetic (AF) coupling can be achieved. The magnetic coupling can be even more reduced ( $< 1meV$ ) by ligating the two FePc molecules with Cl whereby the ground state configuration changes from FM to AF. If the unligated  $(FePc)_2$  is deposited on a Co(001) substrate the lower FePc couples in agreement with previous findings [1,2] FM to the Co film but the intermolecular coupling switches from FM to AF whereby the coupling strength is similar to the one of the free  $(FePc)_2$ .

[1] D. Klar *et al.*, Phys. Rev. B 88, 224424 (2013)[2] H. C. Herper *et al.*, Phys. Rev. B 89, 085411 (2014)

## 15 min. break

MA 16.6 Tue 11:00 EB 202

**Electron correlation in organometallics: insights from density functional theory and exact diagonalization** — SUMANTA BHANDARY<sup>1</sup>, TIM WEHLING<sup>2</sup>, OLLE ERIKSSON<sup>1</sup>, and ●BIPLAB SANYAL<sup>1</sup> — <sup>1</sup>Department of Physics and Astronomy, Uppsala University, Sweden — <sup>2</sup>Institute for Theoretical Physics, University of Bremen, Otto-Hahn-Allee 1, 28359 Bremen, Germany and Bremen Center for Computational Materials Science, University of Bremen, Am Falturm 1, 28359, Bremen, Germany

A proper theoretical description of electronic structure of the 3d orbitals in the metal centers of functional organometallic molecules is a challenging problem. Here, we have used density functional theory and an exact diagonalization method in a many body approach to study the ground state electronic configuration of an iron porphyrin (FeP) molecule. Our study reveals that dynamical correlation effects are important, and FeP is a potential candidate for realizing a spin crossover

due to a subtle balance of crystal field effects, on-site Coulomb repulsion and hybridization between the Fe d-orbitals and ligand N p-states. Moreover, the mechanism of switching between two close lying electronic configurations of Fe-d orbitals is revealed. We discuss the generality of the suggested approach and the possibility to properly describe the electronic structure and related low energy physics of the whole class of correlated metal centered organometallic molecules.

MA 16.7 Tue 11:15 EB 202

**Enhanced magnetic interactions in an lanthanide molecular cluster** — ●KRUNOSLAV PRSA<sup>1</sup>, J. NEHRKORN<sup>1</sup>, S. NEKURUH<sup>1</sup>, W.J. EVANS<sup>2</sup>, J.R. LONG<sup>3</sup>, T. GUIDI<sup>4</sup>, and OLIVER WALDMANN<sup>1</sup> — <sup>1</sup>Physikalisches Institut Universität Freiburg, Germany — <sup>2</sup>Department of Chemistry, University of California, Irvine, USA — <sup>3</sup>Department of Chemistry, University of California, Berkeley, USA — <sup>4</sup>ISIS Facility, STFC Rutherford Appleton Laboratory, United Kingdom

Technological applications of molecular magnets critically depend on the enhancement of their blocking temperatures. Molecules containing rare-earth ions are promising candidates because of strong anisotropy and large individual magnetic moments. However, the first polynuclear lanthanide clusters suffered from a low interaction strength between the magnetic moments. An  $N_2^{3-}$  radical-bridged dinuclear lanthanide molecular complex,  $Tb_2N_2^{3-}$ , was recently synthesized to overcome this problem [1]. Inelastic neutron scattering data on this molecule, its parent compound  $Tb_2N_2^{2-}$  as well as the non-magnetic analogue  $Y_2N_2^{3-}$ , were recorded at the LET instrument at the ISIS neutron source. In addition to the ligand field levels, we observe excitations due to exchange coupling between the lanthanide magnetic moments which present a direct evidence of enhancement of interactions in this system.

[1] J.D. Rinehart *et al.*, Nat. Chem. 538-542 (3), 2011.

MA 16.8 Tue 11:30 EB 202

**X-ray induced demagnetization of single-molecule magnets** — ●JAN DREISER<sup>1,2</sup>, RASMUS WESTERSTRÖM<sup>2,3,4</sup>, CINTHIA PIAMONTEZE<sup>2</sup>, FRITHJOF NOLTING<sup>2</sup>, STEFANO RUSPONI<sup>1</sup>, HARALD BRUNE<sup>1</sup>, SHANGFENG YANG<sup>5</sup>, ALEXEY POPOV<sup>6</sup>, LOTHAR DUNSCH<sup>6</sup>, and THOMAS GREBER<sup>3</sup> — <sup>1</sup>Institute of Condensed Matter Physics, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland — <sup>2</sup>Swiss Light Source, Paul Scherrer Institute, 5232 Villigen, Switzerland — <sup>3</sup>Physik-Institut, Universität Zürich, 8057 Zürich, Switzerland — <sup>4</sup>Department of Physics and Astronomy, Uppsala University, 751 20 Uppsala, Sweden — <sup>5</sup>Hefei National Laboratory for Physical Sciences at Microscale, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China — <sup>6</sup>Department of Electrochemistry and Conducting Polymers, Leibniz Institute of Solid State and Materials Research, 01069 Dresden, Germany

X-ray magnetic circular dichroism measurements on the endohedral single-molecule magnet  $DySc_2N@C_{80}$  [1] at the Dy  $M_{4,5}$  edges exhibit a shrinking of the hysteresis opening with increasing x-ray flux. Our data reveal that this effect can neither be explained by irreversible structural damage nor by a homogeneous temperature rise due to x-ray absorption. The observed large demagnetization cross sections indicate that the resonant absorption of one x-ray photon induces the demagnetization of many molecules [2].

[1] Westerström *et al.*, J. Am. Chem. Soc. **134**, 9840 (2012).

[2] Dreiser *et al.*, Appl. Phys. Lett. **105**, 032411 (2014).

MA 16.9 Tue 11:45 EB 202

**Light-Induced Switching of the Spin of Fe Complexes on Surfaces** — ●MATTHIAS BERNIEN<sup>1</sup>, HOLGER NAGGERT<sup>2</sup>, CHRISTIAN F. HERMANN<sup>1</sup>, FABIAN NICKEL<sup>1</sup>, LUCAS M. ARRUDA<sup>1</sup>, LALMINTHANG KIPGEN<sup>1</sup>, JORGE MIGUEL<sup>1</sup>, ALEX KRÜGER<sup>1</sup>, DENNIS KRÜGER<sup>1</sup>, ENRICO SCHIERLE<sup>3</sup>, EUGEN WESCHKE<sup>3</sup>, FELIX TUCZEK<sup>2</sup>, and WOLFGANG KUCH<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, 14195 Berlin — <sup>2</sup>Institut für Anorganische Chemie, Christian-

Albrechts-Universität zu Kiel, 24098 Kiel — <sup>3</sup>Helmholtz-Zentrum Berlin für Materialien und Energie, 12489 Berlin

Sublimable spin-crossover complexes have recently gained a lot of attention due to their potential application as building blocks for molecular spintronic devices. These molecules possess a metastable spin state that reacts sensitively to tiny perturbations in temperature, light exposure, or intermolecular interactions. If these complexes are immobilized on a solid surface, the spin transition is often quenched. We have studied submonolayers of the Fe(II) spin-crossover complex  $[Fe(bpz)_2(phen)]$  ( $bpz$ =dihydrobis(pyrazolyl)borate,  $phen$ =1,10-phenanthroline) by means of x-ray absorption spectroscopy. Using highly oriented pyrolytic graphite (HOPG) as a weakly interacting substrate we show that even molecules that are in direct contact with a solid surface can undergo a spin-crossover transition as a function of temperature. X-ray magnetic circular dichroism shows that the spin of  $[Fe(bpz)_2(phen)]$  can be switched from  $S = 0$  to  $S = 2$  highly efficiently using green light of 520 nm wavelength at  $T = 5$  K. — Financial support by the DFG (Sfb's 658 and 677) is gratefully acknowledged.

MA 16.10 Tue 12:00 EB 202

**Magnetotransport in carbon nanotube networks: influence of morphology, oxidation, and covalent functionalization with tetranuclear metal complexes** — ●MARLOU SLOT<sup>1</sup>, MICHAEL SCHNEE<sup>2,4</sup>, CLAIRE BESSON<sup>2,3,4</sup>, ROBERT FRIELINGHAUS<sup>2,4</sup>, PAUL KÖGERLER<sup>2,3,4</sup>, CLAUS M. SCHNEIDER<sup>2,4</sup>, and CAROLA MEYER<sup>2,4</sup> — <sup>1</sup>Debye Institute for Nanomaterials Science, Utrecht University, The Netherlands — <sup>2</sup>Peter Grünberg Institut (PGI-6), Forschungszentrum Jülich, Germany — <sup>3</sup>Institut für Anorganische Chemie, RWTH Aachen, Germany — <sup>4</sup>JARA - Fundamentals of Future Information Technologies

Carbon nanotube networks (CNTNs) are a promising material for applications in plastic electronics and spintronics, constituting an electrically and mechanically robust alternative to single CNTs. The range of possible applications is broadened by functionalization. Covalent functionalization with antiferromagnetic tetranuclear metal coordination complexes, facilitated by sidewall oxidation, results in a defined angle of the complex with respect to the tube and a net spin near the CNT.

Low-temperature electrical transport characteristics of the CNTNs, consisting of semiconducting and metallic tubes, exhibit a shift from localized hopping behavior to dominating metallic conduction upon increasing network density. Short thermal oxidation results in an enhanced conductivity. The CNTNs exhibit a negative magnetoresistance (MR). Covalent functionalization with  $\{Co_4\}$ -complexes is observed to affect the magnitude of the MR at low temperatures, which corroborates the influence of these complexes on the transport in the CNTN.

MA 16.11 Tue 12:15 EB 202

**Investigation of hexagonal spin tubes using DMRG** — ●MICHAEL CZOPNIK and JÜRGEN SCHNACK — University of Bielefeld, Germany

The Density Matrix Renormalization Group (DMRG) is one of the most powerful numerical techniques for studying many-body systems. It was developed to overcome the problems arising in the application of the Numerical Renormalization Group (NRG) to quantum lattice many-body systems such as the Hubbard model of strongly correlated electrons.

The physics of spin tubes has attracted much attention in recent years. A so-called "spin tube" is a spin ladder with periodic boundary condition in the rung direction. It has a geometrical frustration in case the number of legs is odd and the frustration induces a variety of interesting phenomena.

We study the ground state and the magnetization of a Heisenberg spin tube made of nickel spins, using Density Matrix Renormalization Group technique (DMRG) and exact diagonalization.

Special emphasis is put on unusual features of the magnetization curve, such as extended plateaus or jumps.