MA 3: Bio- and Molecular Magnetism

Time: Monday 9:30–12:30 Location: EB 202

MA 3.1 Mon 9:30 EB 202

Influence of an intermediate oxygen layer on the magnetic and electronic properties of Fe and Co porphyrin molecules on Cu(001) — •Heike C. Herper[1,3], Mattias Bernien[2], Claudia Weis[1], Carolin Antoniak[1], Bernhard Krumme[1], Jorge Miguel[2], Sumanta Bhandary[3], Biplab Sanyal[3], Dietger Bovenschen[1], Olle Eriksson[3], Peter Entel[1], Wolfgang Kuch[2], and Heiko Wende[1] — [1]Faculty of Physics and CeNIDE, University of Duisburg-Essen, 47048 Duisburg — [2]Institut für Experimentalphysik, Freie Universität Berlin, 14195 Berlin — [3]Department of Physics and Astronomy, Uppsala University, 75120 Uppsala

The ongoing miniaturization of magnetic devices requires the search for new materials, e.g. functional molecules on surfaces. Here, the influence of an intermediate oxygen layer on Cu(001) on the magnetic properties of Fe and Co octaethylporphyrin (OEP) molecules is studied. We have performed a combined study of X-ray absorption spectroscopy (XAS) and density functional theory calculations within the GGA+U method. The calculations reveal that Fe and Co OEP prefer Cu hollow site positions on the oxygen covered surface with an intermediate spin state. The XAS of Co OEP shows a detailed fine structure at the L_3 edge depending on the photon incidence angle. This can be related to the calculated density of states and the occupation of d orbitals with different symmetry. We also investigated the magnetic anisotropy in terms of 2nd order perturbation theory to understand the strong angular dependence of the magnetic dichroic signal of Fe OEP in presence of the oxygen layer. Supported through SFB 491 and SFB 658.

MA 3.2 Mon 9:45 EB 202

Magnetic measurements of a Nickel(II) Double Cubane — •Wolfgang Kroener[1], Andreas Scheurer[2], Klaus Gieb[1], Rolf W. Saalfrank[2], Michael Stocker[1], and Paul Müller[1] — [1]Department of Physics and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg — [2]Department Chemie und Pharmazie, Lehrstuhl für Anorganische und Allgemeine Chemie, Universität Erlangen-Nürnberg

We investigated an octanuclear chloro-bridged nickel(II) double cubane $[(\{\mathrm{Ni}_4^{\mathrm{II}}(\mu_3\text{-OH})\mathrm{Cl}_3(\mathrm{HL})_3\}\mu_2\text{-Cl})_2]$. Single crystal measurements were performed with a custom 2DEG Hall probe magnetometer. Powder measurements were performed with a commercial SQUID magnetometer. Magnetization measurements show two separated hysteresis loops. Temperature as well as sweep-rate dependencies show single-molecule magnet behavior. The loop around zero magnetic field vanishes at 0.9 K, whereas the one at higher fields closes at 1.3 K. This can be explained by anisotropic coupling of the cubane units with $S = 4$. Including this fact into the Hamiltonian, all principal features of the hysteresis curve can be described.

MA 3.3 Mon 10:00 EB 202

Spin densities in high-spin states of Mn(III) and Cu(II) tripelsalen model complexes — •Stefan Leiding[1], Dirk Andrae[2], Andrei Postnikov[3], and Jürgen Schnack[1] — [1]Universität Bielefeld — [2]Freie Universität Berlin — [3]Université de Lorraine, Metz, France

In order to investigate geometric and electronic effects on the ferromagnetic coupling via the spin-polarization mechanism [1], we study heptanuclear complexes related to molecular magnets like $[\{(\mathrm{talen}^{t\text{-}\mathrm{Bu}_2})\text{-}\{\mathrm{Mn}^{\mathrm{III}}(\mathrm{solv})_n\}_3\}_2\{\mathrm{Fe}^{\mathrm{III}}(\mathrm{CN})_6\}]^{3+}$ [2] and their fragments with Kohn-Sham density functional theory. Conjugated double bonds in these complexes affect the magnetic properties, like the spin polarization, mainly due to the switch in sequence of highest occupied molecular orbitals corresponding to two spin components. In order to identify, in each case, the state with the lowest energy, we carefully studied the effect of imposing, and lifting, the symmetry constraints specific to the molecular fragment in question onto the molecular orbitals.

[1] J. Cano, E. Ruiz, S. Alvarez, M. Verdaguer, Comments Inorg. Chem. **20** (1998) 27; [2] T. Glaser, M. Heidemeier, E. Krickemeyer, H. Bögge, A. Stammler, R. Fröhlich, E. Bill, J. Schnack, Inorg. Chem. **48** (2009) 607.

MA 3.4 Mon 10:15 EB 202

Magnetocaloric properties of gadolinium based heterometallic molecules studied by the finite-temperature Lanczos method — Christian Heesing[1], Oliver Wendland[1], Thomas N. Hooper[2], Euan Brechin[2], and •Jürgen Schnack[1] — [1]Universität Bielefeld, Universitätsstr. 25, D-33615 Bielefeld — [2]School of Chemistry, University of Edinburgh, Edinburgh, U.K.

The magnetocaloric effect enables one to heat or cool by varying the applied magnetic field. Magnetic molecules with a high density of low-lying high spin multiplets are especially desirable in this context since they lead to big entropy changes when sweeping the field isothermally. In this contribution we discuss gadolinium based heterometallic molecules that have been modeled by means of the finite-temperature Lanczos method [1]. This method generates very accurate approximations of thermal observables for Hilbert space dimensions of up to 10^{10}.

[1] J. Schnack, O. Wendland, Eur. Phys. J. B **78** (2010) 535-541

MA 3.5 Mon 10:30 EB 202

Coherent Manipulation of Electron Spins in a {Cu3} Spin Triangle Complex — •Choi K.-Y.[1], Kumar P.[2], Lemmens P.[2], Bassil B. S.[3], Kortz U.[3], Nojiri H.[4], Wang Z. X.[5], Tol J. van[5], and Dalal N. S.[5] — [1]Dpt. Physics, Chung-Ang Univ., Seoul, Korea — [2]IPKM, TU-BS, Germany — [3]Jacobs Univ., Bremen, Germany — [4]IMR, Tohoku Univ., Sendai, Japan — [5]NHMFL/FSU, Tallahassee, USA

Molecular magnets have been proposed as a promising candidate for spin-based qubits. As a test bed toward scalable qubits, we explore the isosceles antiferromagnetic spin triangle {Cu3-X} (X=As, Sb) impregnated in free standing nanoporous silicon. By using 240 GHz microwave pulses Rabi oscillations were observed and a spin memory time was measured to be T2=1066 ns at 1.5 K. This demonstrates that this hybrid material provides a promising scheme for implementing spin-based quantum gates. Comparing samples with different symmetries and environments we give evidence that spin chirality is the main decoherence source of spin triangle molecules unlike other molecular magnets. Acknowledgement: DFG and NTH

MA 3.6 Mon 10:45 EB 202

Propagation of spin information at supra-molecular scale through hetero-aromatic linkers — •Valerio Bellini[1], Th. B. Faust[2], G. A. Timco[2], G. Lorusso[1], A. Candini[1], F. Tuna[2], E. J. L. McInnes[2], R. G. Pritchard[2], S. J. Teat[3], W. Wernsdorfer[4], R. E. P. Winpenny[2,5], and M. Affronte[1,6] — [1]CNR - Istituto di Nanoscienze - S3, Modena, Italy — [2]School of Chemistry, The University of Manchester, Manchester, UK — [3]ALS, LBNL, Berkeley, USA — [4]Laboratoire L. Néel, Grenoble, France — [5]The Photon Science Institute, The University of Manchester, Manchester, UK — [6]Dipartimento di Fisica, Università di Modena e Reggio Emilia, Modena, Italy

By density-functional theory calculations, we rationalize the behavior of a series of $\mathrm{Cr_7Ni}$ dimers for which we are able to systematically change the aromatic linker thus tuning the strength of the magnetic interaction, as shown by EPR and microSQUID measurements [1,2]. We also predict a $\cos^2$ dependence of the magnetic coupling on the twisting angle between the aromatic cycles [3], a mechanism parallel to charge transport on similar systems [4]. These findings pave the way for a whole series of possible experimental investigations, by systematically varying the organic bridges and the magnetic frontier atoms, in order to tune and choose the appropriate coupling regime.

[1] F. Troiani, V. Bellini, et al., Nanotechnology 21, 274009 (2010). [2] V. Bellini, et al., Phys. Rev. Lett. 106, 227205 (2011). [3] Th. B. Faust, V. Bellini, et al., Published on line in Chem.-Eur. J. (2011) [DOI:10.1002/chem.201101785]. [4] L. Venkataraman, et. al., Nature 442, 904 (2006).

15 min. break

MA 3.7 Mon 11:15 EB 202

Magnetic coupling between metalloporphyrins and Ni films across a graphene sheet — •Christian Felix Hermanns[1], Kartick Tarafder[2], Mattias Bernien[1], Alex Krüger[1], Yin-Ming Chang[1], Anton Bruch[1], Peter Oppeneer[2], and Wolfgang Kuch[1] — [1]Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — [2]Department of Physics and Astronomy, Uppsala University, P.O. Box 516, S-75120 Uppsala, Sweden

We report on a combined experimental-theoretical study of Co and Fe octaetylporphyrin (CoOEP and FeOEP) molecules on a graphene sheet, supported by a ferromagnetic (FM) Ni film on W(110). Consistent with the results of angle-dependent X-ray absorption spectroscopy (XAS) at the N K edge, density functional theory (DFT+U) calculations show that both, CoOEP and FeOEP molecules, adsorb flat on the surface, while the porphyrine macrocycles are distorted due to the interaction with the substrate. By means of X-ray magnetic circular dichroism measurements at the Co and Fe $L_{2,3}$ edges we show that the FM Ni film induces a magnetic order on the Co and Fe ions of the porphyrins. According to DFT+U calculations the underlying mechanism is an indirect exchange coupling across the graphene layer. Angle dependent Co and Fe $L_{2,3}$ XA spectra resemble those of free molecules, indicating a physisorption of the metalloporphyrins. This is in line with the calculated distances between the porphyrins and the graphene plane of more than 3 Å for both types of metalloporphyrins. This work is supported by the DFG (Sfb 658), the Swedish-Indian Research Link Programme, the C. Tryggers Foundation, and the SNIC.

MA 3.8 Mon 11:30 EB 202

Direct observation of a ferri-to-ferromagnetic transition in a fluoride-bridged 3d-4f molecular cluster — •Jan Dreiser[1], Kasper S. Pedersen[2], Cinthia Piamonteze[1], Stefano Rusponi[3], Zaher Salman[1], Md. Ehesan Ali[4], Magnus Schau-Magnussen[2], Christian Aa. Thuesen[2], Stergios Piligkos[2], Hoegni Weihe[2], Hannu Mutka[5], Oliver Waldmann[6], Peter Oppeneer[7], Jesper Bendix[2], Frithjof Nolting[1], and Harald Brune[3] — [1]Paul Scherrer Institut, 5232 Villigen PSI, Switzerland. — [2]Dep. of Chemistry, Univ. of Copenhagen, 2100 Copenhagen, Denmark. — [3]Institute of Condensed Matter Physics, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland. — [4]Center f. Theoretical Chemistry, Ruhr-Univ. Bochum, 44801 Bochum, Germany. — [5]Institut Laue-Langevin, 38042 Grenoble, France. — [6]Physikalisches Institut, Univ. Freiburg, 79104 Freiburg, Germany. — [7]Dep. of Physics and Astronomy, Uppsala Univ., 751 20 Uppsala, Sweden.

We report on a X-ray magnetic circular dichroism (XMCD) study of the novel fluoride-bridged molecular nanomagnet DyCrDy. Element-specific magnetization curves allow us to directly observe the field-induced transition from a ferrimagnetic to a ferromagnetic arrangement of the Dy and Cr magnetic moments. By fitting a spin-Hamiltonian model to the XMCD data we extract the strength of the Dy-Cr exchange coupling. The value found from XMCD is consistent with SQUID magnetometry and inelastic neutron scattering measurements. Furthermore, based on this approach we investigate other 3d-4f molecular nanomagnets.

MA 3.9 Mon 11:45 EB 202

Ab initio inspection of magnetic and redox bistability — •Mikaël Kepenekian — CIN2, Bellaterra, Spain

Molecular materials have stimulated intense experimental and theoretical work over the last decades. Indeed, the nature of these materials allows one to take advantage of the chemical engineering in order to design systems of interest. After achievements in the fields of magnetism and conduction, molecular materials are now sought as they can associate these properties. Nevertheless, the simulation of such materials remains a problem since (i) different energetic scales are involved, and (ii) the mono-reference nature of DFT-based calculations prevent from an accurate description of properties such as magnetism. In contrast, multi-reference wavefunction-based calculations offer the opportunity to work with proper spin-states, and give access to excited states. These methods have proven their ability to provide a quantitative agreement with experience, particularly in the field of molecular magnetism.

In this work, we used multi-reference ab initio calculations to investigate the microscopic origin of the behavior exhibited by bistable molecular materials. Starting from the inspection of spin-crossover complexes we were able not only to identify a microscopic origin of the spin-crossover phenomenon but also to quantify the magnitude of the hysteresis width. More sophisticated scenario involving the simultaneous spin and charge distribution change can also be anticipated in porphyrin-based system. At the molecular level, the requirements for bistability can be foreseen and specific target objects can be proposed in the light of the electronic and structural modifications.

MA 3.10 Mon 12:00 EB 202

Quantized Ferromagnetic Spin Waves in Mn$_7$-Disks Identified by their Q Dependence in Inelastic Neutron Scattering Experiments — •Joscha Nehrkorn[1], Oliver Waldmann[1], Shreya Mukherjee[2], George Christou[2], Thierry Strässle[3], and Hannu Mutka[4] — [1]Physikalisches Institut, Universität Freiburg, Germany — [2]Department of Chemistry, University of Florida, USA — [3]LNS, ETH Zürich & Paul Scherrer Institut, Switzerland — [4]Institut Laue-Langevin, France

The concept of ferromagnetic spin waves was developed for extended systems in the early days of quantum mechanics and since then successfully applied in many cases. By limiting the number of spin centers the excitation spectrum becomes quantized. The quantized ferromagnetic spin wave (QFSW) model allows us to calculate those excitations of ferromagnetically coupled molecular nanomagnets exactly, which can be observed by inelastic neutron scattering (INS) at low temperatures. Such systems are an example of many-body physics in clusters containing only a few magnetic centers.

The two disk-like molecules Mn$_7$11 and Mn$_7$16 have an almost identical magnetic core. Surprisingly the exchange of a peripherical ligand changes the ground state spin from $S = 11$ for Mn$_7$11 to the maximal possible value $S = 16$ for Mn$_7$16. We studied them with INS on the spectrometers IN5 (ILL) and FOCUS (PSI). The ability of INS to probe the wave functions via the Q dependence allows us to identify the observed excitations as QFSW excitations. This fact was essential to model the magnetic properties of the two disks correctly.

MA 3.11 Mon 12:15 EB 202

Different magnetization blocking mechanisms in 3d4f heterometallic single-molecular magnets; an experimental study — •Alexander Sundt[1], K. C. Modal[2], Y. Lan[2], C. E. Anson[2], L. Ungur[3], A. K. Powell[2], L. Chibotaru[3], and Oliver Waldmann[1] — [1]Physikalisches Institut, Universität Freiburg — [2]Institute of Inorganic Chemistry, Karlsruhe Institute of Technologie — [3]Devision of Quantum and Physical Chemistry and INPAC, Katholieke Universiteit Leuven

The observation of slow relaxation and quantum tunneling of the magnetization at very low temperatures in the molecule Mn_{12} in 1993 opened the research field of single molecular magnets (SMM). Recently heterometallic SMMs of transition metal and rare earth ions have been a focus of research as the single-ion anisotropy and the large angular momentum of the rare earth ions is believed to positively contribute to the energy barrier U_{eff} for magnetization reversal. Relaxation studies reveal the presence of unexpected additional thermal relaxation process in these clusters.

In this talk we present magnetic studies on heterometallic clusters containing Dy^{III}, a highly anisotropic rare earth ion. DC magnetization, AC susceptibility, and magnetization relaxation data are recorded on e.g. the cluster Co_2Dy_2 for different temperatures, fields and AC frequencies. The experimental data show a crossover of the blocking mechanism for magnetization reversal with temperature. Our careful analysis allows us to determine them as an exchange- and a single-ion-based relaxation mechanism. Further systems will also be discussed.