

MA 20: Bio- and Molecular Magnetism

Time: Tuesday 9:30–13:00

Location: HSZ 301

MA 20.1 Tue 9:30 HSZ 301

Changing the Molecular Conformation of Endohedral Rare Earth Single-Molecule Magnets with Magnetic Torque —

•ARAM KOSTANYAN¹, RASMUS WESTERSTRÖM², YANG ZHANG³, ALEXEY POPOV³, and THOMAS GREBER¹ — ¹Physik-Institut, Uni Zürich, Winterthurerstr. 190, 8057 Zürich, Switzerland — ²Division of Synchrotron Radiation Research, Department of Physics, Lund University, Lund, Sweden — ³Nanoscale Chemistry, IFW Dresden, Helmholtzstr. 20, 01069, Dresden, Germany

The endohedral unit of endohedral fullerenes exhibits thermally activated hopping motion between low-energy conformations. The motion ceases out at low temperatures locking the unit in a random state.

For single-molecule magnet HoLu₂N@C₈₀, the magnetic moment of Ho is aligned with the Ho-N axis due to strong ligand field imposed by the N³⁻ ion. If the external magnetic field applies a torque on the magnetic moment of the Ho³⁺ ion it can be transferred to the encapsulated unit.

Field and temperature dependent measurements show a conformational change by means of magnetic torque on a single magnetic moment. At 1.8 K, the in-field cooled sample shows a magnetization curve that exceeds that of the zero-field cooled one. The difference does not scale with a single factor and increases with decreasing temperature sweep rate.

By means of a first order kinetics model, it is possible to determine the attempt frequency and activation energy for the hopping motion. It also allows to understand the non-linear field dependence of the effect.

MA 20.2 Tue 9:45 HSZ 301

High-frequency electron paramagnetic resonance investigation of transition metal complexes – Ni monomer and Ni₂ dimer complexes as single-molecule magnets —

•SVEN SPACHMANN¹, CHANGHYUN KOO¹, MSIA TAVHELIDSE¹, CEBRAIL PÜR¹, ROLAND BISCHOFF², MANUEL REH², HANS-JÖRG KRÜGER², and RÜDIGER KLINGELER^{1,3} — ¹Kirchhoff Institute for Physics, Heidelberg University, Heidelberg, Germany — ²Faculty of Chemistry, TU Kaiserslautern, Kaiserslautern, Germany — ³Center for Advanced Materials, Heidelberg University, Heidelberg, Germany

The magnetic properties of a Ni(II) monomer and a Ni(II)₂ dimer with a negatively charged radical bridge ligand are studied by means of high-frequency electron paramagnetic resonance (HF-EPR). The g-factors and the spin ground states of both complexes are unambiguously determined from the spectra: $g = 2.126$, $S = 5/2$ for the dimer, and $g = 2.115$, $S = 1$ for the monomer. Significant zero-field splitting and equally separated resonance features in the EPR spectra indicate the magnetic anisotropy of both complexes. Modelling the experimental data by an appropriate spin Hamiltonian reveals an axial-type anisotropy $|D| = 0.85$ K for the dimer and a plane-type anisotropy $|D| = 4.52$ K for the monomer. The results are compared to similar Ni₂ dimer complexes and the contributions of the different radical bridge ligands to the magnetic anisotropy are discussed.

MA 20.3 Tue 10:00 HSZ 301

Switching of a spin-crossover molecule on a surface —

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Spin-crossover (SCO) complexes contain a transition metal ion that can be switched between a low-spin and a high-spin state by external stimuli. An adsorbed SCO complex couples to the substrate and consequently may change its spin-switching property. Using low temperature scanning tunneling microscopy we investigated the SCO-compound [Fe(pap)₂]⁺ClO₄⁻ (pap= N-2-pyridylmethylidene-2-hydroxyphenylaminato) on substrates with supposedly different couplings to the molecule, namely Au(111), Cu(001) and Cu₂N/Cu(001). Although we made various attempts, we found no indication of any STM tip induced modifications of Fe(pap)₂ on Au and Cu. By contrast, single Fe(pap)₂ on Cu₂N can be reproducibly and reversibly switched. We observed three states that exhibit different shapes in images and different spectroscopic features. We discuss the data in

terms of conformational changes as well as spin-state modifications. Financial support by the SFB 677 is gratefully acknowledged.

MA 20.4 Tue 10:15 HSZ 301

High-frequency EPR study on the 3d-4f heterometallic single crystal DyNi₂ —

•CHANGHYUN KOO¹, MSIA TAVHELIDSE¹, MICHAEL GROSSHAUSER², DENNIS MÜLLER², PETER COMBA², and RÜDIGER KLINGELER^{1,3} — ¹Kirchhoff Institute of Physics, Heidelberg University, Germany. — ²Institute of Inorganic Chemistry, Heidelberg University, Germany. — ³Center for Advanced Materials, Heidelberg University, Germany.

3d-4f heterometallic complexes provide a potential route to highly anisotropic single molecular magnets with high magnetic moments. Here, we report on the static and dynamic magnetic properties of a heterometallic [Dy^{III}(Ni^{II}(L^{tacn}))₂]ClO₄ (i.e., DyNi₂) single crystal. The spin ground state is derived from the static magnetisation data. Due to misaligned magnetic axes of the magnetic ions and twisted misaligned two molecules in the unit cell, our high-frequency electron paramagnetic resonance (HF-EPR) spectra exhibit non-equally separated resonance features including a forbidden transition in a resonance frequency-magnetic field diagram. From the temperature dependence of the resonances, the ground state transitions and the excited state transitions are sorted out. The comparison of experimental data with simulations by means of matrix diagonalization of an appropriate spin Hamiltonian including an Ising concept for the Dy ion allows reasonably estimating the relevant parameters, i.e. D , E , of the Ni ions, and $J_{\text{Dy-Ni}}$ in the DyNi₂ complex.

MA 20.5 Tue 10:30 HSZ 301

Magnetic properties of free transition-metal-benzene complexes —

•CHRISTINE BÜLOW^{1,2}, VICENTE ZAMUDIO-BAYER^{1,3}, REBECCA LINDBLAD^{1,4}, MARTIN TIMM¹, AKIRA TERASAKI⁵, BERND VON ISSENDORFF³, and TOBIAS LAU¹ — ¹Helmholtz-Zentrum Berlin, Berlin, Germany — ²Technische Universität Berlin, Berlin, Germany — ³Universität Freiburg, Freiburg, Germany — ⁴Lund University, Lund, Sweden — ⁵Kyushu University, Fukuoka, Japan

MnBz₂⁺ (Bz = benzene) is a very stable 18 valence electron system. Theory and indirect experimental evidence indicate either the expected fully quenched or a surprising fully atomic-like spin magnetic moment. For CrBz₂⁺, which is one electron short of the closed electronic shell, a magnetic moment of either 1 μ_B or 5 μ_B is predicted.

We have investigated the magnetic and electronic properties of MnBz_n⁺ and CrBz_n⁺ ($n = 0 - 2$) in the gas phase by x-ray magnetic circular dichroism and x-ray absorption spectroscopy in a cryogenic ion trap. Our results show that 3d electrons in MnBz and CrBz are localized and therefore these complexes carry a magnetic moment whereas in MnBz₂⁺ and CrBz₂⁺ the 3d electrons are delocalized and the 3d magnetic moment is quenched.

MA 20.6 Tue 10:45 HSZ 301

Magnetism of highly-ordered two-dimensional arrays of Fe₄ on graphene —

•FABIAN PASCHKE¹, LUCA GRAGNANIELLO¹, PHILIPP ERLER¹, PETER SCHMITT², NICOLE BARTH¹, SABINA SIMON¹, HARALD BRUNE³, STEFANO RUSPONI³, and MIKHAIL FONIN¹ — ¹Department of Physics, University of Konstanz, Germany — ²Department of Chemistry, University of Konstanz, Germany — ³Institute of Condensed Matter Physics, École Polytechnique Fédérale de Lausanne, Switzerland

We demonstrate that electrospray deposition enables the fabrication of highly-periodic 2D arrays of Fe₄H single molecule magnets on graphene/Ir(111). From the magnetic field dependence of the x-ray magnetic circular dichroism signal, we infer that the magnetic easy axis of each Fe₄H molecule is oriented perpendicular to the sample surface with the value of the uniaxial anisotropy being unaffected upon the deposition on graphene. Furthermore, we observe inelastic features in STS, due to spin-flip excitations from the magnetic ground state, giving access to the intramolecular exchange coupling J_1 on the single-molecule level, which is unprecedentedly close to the bulk value. Our findings suggest that Fe₄H molecules undergo only negligible interaction with the graphene/Ir(111) substrate, making it possible to build a well-defined two-dimensional system with preserved magnetic properties as compared to bulk.

15 min. break.

MA 20.7 Tue 11:15 HSZ 301

Magnetic properties of EuCot nanowires on graphene/Ir(111) — ●NICO ROTHENBACH¹, FELIX HUTTMANN², KATHARINA OLLEFS¹, STEFAN KRAUS², MATTHIAS BERNIEN³, LUCAS M. ARRUDA³, FABIAN NICKEL³, ANDREW J. BRITTON³, WOLFGANG KUCH³, THOMAS MICHELY², and HEIKO WENDE¹ — ¹University of Duisburg-Essen and CENIDE — ²University of Cologne — ³Freie Universität Berlin

Magnetic coupling and the magnetic anisotropy of localized 4f magnetic moments connected via organic ligands in molecular networks are a highly topical field of research owing to potential applications in organic spintronics [1-3]. We investigated organometallic sandwich-molecular nanowires of europium-cyclooctatetraene (EuCot) on graphene/Ir(111) by means of x-ray magnetic circular dichroism (XMCD) down to 2.5 K. Using temperature-, angular-, and field-dependent europium $M_{4,5}$ -edge XMCD measurements we studied two different coverages, namely 0.5 and 2.0 monolayers (ML) of EuCot. The comparison of the XMCD spectra of the submonolayer EuCot sample with the multilayer sample shows pronounced differences, resulting in different orbital moments. Furthermore, for the submonolayer coverage we determine a clearly different functional behavior of the field-dependent XMCD data for normal and grazing x-ray incidence, whereas no anisotropic behavior is found for the 2.0-ML sample.

[1] P. Gambardella et al., Nature Materials 8, 189 (2009)

[2] A. Lodi Rizzini et al., Surface Science 630, 361 (2014)

[3] Y. Lan et al., J. Mater. Chem. C 3, 9794 (2015)

MA 20.8 Tue 11:30 HSZ 301

Formation of metallofullerene magnetic arrays: theoretical perspectives. — ●STANISLAV AVDOSHENKO and ALEXEY POPOV — Institute for Solid State Research, IFW, Dresden

Modeling of formation and properties self-assembled monolayer (SAM) is a very challenging task, especially if highly functional-ligands are concerned. It is true, for instance, in the case of endohedral metallofullerene (EMF) based SAM - promising single molecular magnets (SMMs) grids in-making. Properties of such SMM grids would be a function of SAM architecture (attachment types and crowding effects) and innercluster dynamics under these geometrical constraints. Electronic structure complexity of EMFs and structural mobility of ligands in SAMs brings a dual issue. On the one hand, a minimal level of theory to address the magnetic properties of the systems would require "complete active space"- quality methods. On the other hand, while the system dynamic can be approached by less computationally demanding semiclassical or even classical approaches, such methods are unable to give a reliable magneto-physics of the SMM unit. In our report, we will offer a set of concepts to deal with this problem by extensive development of the multiscale methods (MSM), in which the whole system is divided into the regions described with different levels of theory accordingly to its complexity.

MA 20.9 Tue 11:45 HSZ 301

Recent development of endohedral metallofullerenes for single molecule magnetism — ●ALEXEY POPOV¹, DENIS KRYLOV¹, FUPIN LIU¹, LUKAS SPREE¹, STANISLAV AVDOSHENKO¹, ARAM KOSTANYAN², and THOMAS GREBER² — ¹Nanoscale Chemistry, Leibniz Institute for Solid State and Materials Research (IFW Dresden), Helmholtzstrasse 20 01069, Dresden, Germany — ²Physik-Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

The molecules of endohedral metallofullerenes (EMFs) comprise the fullerene cage encapsulating metal ions (usually lanthanides). Metal atoms donate their valence electrons to the fullerene cage resulting in ionic environment, and Coulomb repulsion between metal atoms can be balanced by a presence of negatively charged non-metals. This results in a large magnetic anisotropy with quasi-uniaxial ligand field, which leads to the single molecule magnet (SMM) behaviour of lanthanide-based EMFs. When more than one lanthanide ion is encapsulated, the intracluster exchange and dipolar interactions have dramatic effect on the magnetic properties.

Here we will discuss the progress in the synthesis and magnetic properties of endohedral metallofullerenes. Different type of endohedral clusters (nitride, carbide, sulfide) as well as dimetallofullerenes will be considered and the influence of central non-metal atoms on magnetic anisotropy of lanthanides and intracluster exchange interaction will be analyzed. The route to EMF-SMMs with high blocking temperatures will be outlined.

MA 20.10 Tue 12:00 HSZ 301

Efficient ab-initio treatment of magnetism in metal organic frameworks — ●KAI TREPTE¹, SEBASTIAN SCHWALBE², JENS KORTUS², and GOTTHARD SEIFERT¹ — ¹Technische Universität Dresden, Theoretical Chemistry, Germany — ²Technische Universität Bergakademie Freiberg, Institute for Theoretical Physics, Germany

Metal organic frameworks (MOFs) contain specific metal centers as a secondary building unit (SBU) which are interconnect via organic linkers to form three-dimensional networks. An example of a magnetic MOFs is DUT-8(Ni) (DUT - Dresden University of Technology), where the SBUs are Ni dimers. Initially, we studied the magnetic ground state of the crystalline system [1], which turns out to be antiferromagnetic. Considering that MOFs tend to have rather large unit cell (> 100 atoms), we generated a set of model systems (< 30 atoms) which are based on the crystalline structures. These models represent the magnetic properties of the crystals while drastically reducing computational time. Additionally, modifications on the models are easy to implement, allowing the study of different chemical environments or other metal centers and the effect on the magnetic coupling [2]. These investigations show that it is possible to introduce a ferromagnetic/high-spin (HS) coupling into the original system.

[1] Treppe et al., PCCP, vol. 17, pp. 17122-17129, 2015

[2] Schwalbe et al., PCCP, vol. 18, pp. 8075-8080, 2016

MA 20.11 Tue 12:15 HSZ 301

Influence of intermolecular interactions on magnetic observables — ●JÜRGEN SCHNACK — Universität Bielefeld, Fakultät für Physik, Universitätsstr. 25, D-33615 Bielefeld

Very often it is an implied paradigm of molecular magnetism that magnetic molecules in a crystal interact so weakly that measurements of dc magnetic observables reflect ensemble properties of single molecules. But the number of cases where the assumption of virtually noninteracting molecules does not hold grows steadily. A deviation from the noninteracting case can especially clearly be seen in clusters with antiferromagnetic couplings, where steps of the low-temperature magnetization curve are smeared out with increasing intermolecular interaction. In this contribution we demonstrate with examples in one, two, and three space dimensions how intermolecular interactions influence typical magnetic observables such as magnetization, susceptibility, and specific heat.

[1] J. Schnack, Phys. Rev. B **93** (2016) 054421

MA 20.12 Tue 12:30 HSZ 301

Inelastic Neutron Scattering and Mössbauer Spectra of a Novel Spin Frustrated Fe₇-Propeller — ●SIYAVASH NEKURUH¹, K. PRSA¹, I. KÜHNE², C.E. ANSON², A.K. POWELL², and O. WALDMANN¹ — ¹Physikalisches Institut, Universität Freiburg, Germany — ²Institut für Anorganische Chemie, Karlsruhe Institut für Technologie (KIT)

Among the series of hepta-nuclear Fe^{III} molecular complexes with disk shape, the molecule [Fe₇^{III}(Cl)(MeOH)₆O₃(OMe)₆(PhCO₂)₆]Cl₂, or Fe₇ in short, is exceptional: It exhibits a unique antiferromagnetic exchange topology, which is reminiscent of a three-bladed propeller, giving rise to spin frustration.

We here present a study of the magnetic excitations in Fe₇ by inelastic neutron scattering (INS), and Mössbauer spectroscopy. The INS spectra exhibit three features at energies of 0.27, 0.57 and 1 meV, which from T and Q dependence are of magnetic origin. Field dependent Mössbauer spectra could be fitted to two well defined and distinct sextets, one of the sextets was assigned to the central Fe ion and the other to the six peripheral Fe ions. The Mössbauer data allow us to extract the respective local Fe spin densities, providing additional insight in the spin frustration in the molecule.

MA 20.13 Tue 12:45 HSZ 301

Polarized inelastic neutron scattering study of a single-molecule magnet Mn₅ — ●KRUNOSLAV PRSA¹, HUI-LIEN TSAI², HANNU MUTKA³, PASCALE DEEN⁴, and OLIVER WALDMANN¹ — ¹Physikalisches Institut Universität Freiburg, Germany — ²Department of Chemistry, National Cheng Kung University, Tainan, Taiwan — ³Institut Laue Langevin, 6 Rue Jules Horowitz, B.P. 156, 38042 Grenoble, Cedex 9, France — ⁴European Spallation Source, Tunavägen 24, 223 63 Lund, Sweden

The polarized inelastic neutron scattering technique extends the usual non-polarized variety by being able to discern between the vibrational

and magnetic signals. We show results of inelastic neutron scattering study on a conventional 3d-element single-molecule magnet Mn₅ [1]. The non-polarized data taken at the IN5 spectrometer reveal five peaks with additional broader features in the spectrum: I at 0.38 meV, II at 0.55 meV, III at 1.9 meV and IV at 3.8 meV and V at 7.7 meV. Based on the temperature dependence, the peak I is clearly a cold magnetic peak, while for the other peaks the assignment was less obvious. A subsequent polarized experiment at the D7 spectrometer directly

proved the magnetic origin of the peak III. In addition, the polarization analysis of the elastic channel enabled extraction of the pure nuclear scattering that confirmed the persistence of the crystal structure upon cooldown. Together with the published thermodynamical data [1], these results have allowed us to determine the parameters of the microscopic Hamiltonian of the system.

[1] C-I. Yang *et. al.*, JACS 456-457 (**129**), 2007.