

MA 33: Biomedical and molecular magnetism

Time: Wednesday 15:00–18:00

Location: H 1012

MA 33.1 Wed 15:00 H 1012

Pictorial description of elementary excitations in ferromagnetic molecular magnets — ●KRUNOSLAV PRSA and OLIVER WALDMANN — Physikalisches Institut, Universität Freiburg, Germany

The common spin-wave approximation of many-body effects in magnetic solids can be used to describe excitations from the ferromagnetic ($S = S_{max}$) ground state in molecular magnets. Starting from the Heisenberg Hamiltonian, both the classical and the quantum approaches provide exact solutions of the transitions from the ground state into the $M = M_{max} - 1$ sector, which are observed in neutron scattering experiments at low temperatures. With the help of the classical approach we infer pictorial descriptions of the magnon wavefunctions similar to the illustrations of the vibrational normal modes in molecules. The magnetic normal modes correspond to a set of standing waves of precession around the polarized ground state. We argue that this representation leads to a better intuitive understanding of the excitations, their symmetry properties, and has links to the energy and wavevector dependence of intensity in the neutron scattering experiments.

MA 33.2 Wed 15:15 H 1012

First principle determination of spin-phonon coupling mechanism in single molecule magnets — ●ALESSANDRO LUNGH¹, FEDERICO TOTTI², ROBERTA SESSOLI², and STEFANO SANVITO¹ — ¹School of Physics, CRANN and AMBER, Trinity College Dublin, Dublin 2, Ireland — ²Dipartimento di Chimica "Ugo Schiff", Università degli studi di Firenze, Sesto F.no, Italy

Single molecule magnets (SMMs) have been extensively investigated for about twenty years and a detailed knowledge of the physical laws at the origin of their static spin properties is now largely achieved. However, still little is known about the microscopic origin of the relaxation processes involved in the spin dynamics. The main interaction responsible for spin relaxation at finite temperature is the spin-phonon coupling and first-principles atomistic theory offers a natural tool to study such interaction. In this contribution, we will present a formalism for the spin-phonon dynamics suitable for its implementation together with post Hartree-Fock and Density Functional Theory calculations. We will illustrate the application of such formalism to describe the spin relaxation of the Fe(tpa)Ph SMM[1]. Results of these simulations will be illustrated with emphasis on the temperature dependence of the spin relaxation [2] and on the nature of the phonons primarily responsible for the relaxation in molecular spin systems [3].

[1] W. H. Harman et al., J. Am. Chem. Soc., 2010, 132, 1224. [2] A. Lunghi, F. Totti, R. Sessoli, S. Sanvito, Nat. Commun., 2017, 8, 14620 [3] A. Lunghi, F. Totti, S. Sanvito, R. Sessoli, Chem. Sci., 2017, 8 (9), 6051-6059.

MA 33.3 Wed 15:30 H 1012

spin-reversal energy barriers of 305 K for Fe²⁺ d⁶ ions with linear ligand coordination — ●ZIBA ZANGENEHPOURZADEH¹, LEI XU¹, RAVI YADAV¹, STANISLAV AVDOSHENKO¹, JEROEN VAN DEN BRINK¹, ANTON JESCHE², and LIVIU HOZOI¹ — ¹IFW Dresden, Helmholtzstr. 20, 01069 Dresden, Germany — ²Center for Electronic Correlations and Magnetism, Augsburg University, 86135 Augsburg, Germany

A remarkably large magnetic anisotropy energy of 305 K is computed by quantum chemistry methods for divalent Fe²⁺ d⁶ substitutes at Li-ion sites with D_{6h} point-group symmetry within the solid-state matrix of Li₃N. This is similar to values calculated by the same approach and confirmed experimentally for linearly coordinated monovalent Fe¹⁺ d⁷ species, among the largest so far in the research area of single-molecule magnets. Our *ab initio* results therefore mark a new exploration path in the search for superior single-molecule magnets, rooted in the $d_{xy}^{1.5}d_{x^2-y^2}^{1.5}d_{z^2}^1d_{yz}^1d_{zx}^1$ configuration of d⁶ transition-metal ions with linear nearest-neighbor coordination. This d⁶ axial anisotropy may be kept robust even for symmetries lower than D_{6h} , provided the ligand and farther-neighbor environment is engineered such that the $d_{xy}^{1.5}d_{x^2-y^2}^{1.5}d_{z^2}^1d_{yz}^1d_{zx}^1 - d_{xy}^1d_{x^2-y^2}^1d_{z^2}^2d_{yz}^1d_{zx}^1$ splitting remains large enough[1].

[1] Nanoscale **9**, 10596 (2017).

MA 33.4 Wed 15:45 H 1012

High Spin Cycles: Topping the Spin Record for a Single Molecule verging on Quantum Criticality — ●JÜRGEN SCHNACK — Universität Bielefeld, PF 100131, D-33501 Bielefeld

Theory predicts a number of interesting quantum critical phenomena for low-dimensional magnetic systems, where the ground state and thus low-temperature properties of a material change drastically upon even a small variation of an appropriate external parameter. Here we report a mixed 3d/4f cyclic coordination cluster that turns out to be very near or even at such a quantum critical point. The molecule forms a nano-torus with alternating gadolinium and iron ions with a nearest neighbor Fe-Gd coupling and a frustrating next-nearest neighbor Fe-Fe coupling. Such a spin arrangement corresponds to a cyclic delta or saw-tooth chain, which can exhibit a variety of frustration effects, among them giant magnetization jumps as well as macroscopic degeneracies of the ground state with profound caloric consequences. The present cluster is situated on the ferromagnetic side of the Quantum Critical Point with a ground state spin of S=60, which makes it simultaneously the magnetic molecule with the largest total spin ever observed for a magnetic molecule.

MA 33.5 Wed 16:00 H 1012

Magnetic properties of novel single molecule magnets: Lanthanide dimetallofullerenes — ●GEORGIOS VELKOS, DENIS KRYLOV, FUPIN LIU, LUKAS SPREE, and ALEXEY POPOV — Leibniz Institute for Solid State and Materials Research, Helmholtzstrasse 20, 01069 Dresden, Germany

The encapsulation of two lanthanide atoms inside a fullerene (carbon cage) creates a unique environment for the formation of a single-electron metal-metal bond between the endohedral lanthanide ions. Giant exchange coupling between 4f-based magnetic moments of the lanthanide ions and the spin of an unpaired electron gives a large 'superspin' persistent to room temperature. Single molecule magnetism with large blocking temperature of magnetization has been recently discovered in Dy₂@C₈₀. In this work, we further explore the concept of coupling localized magnetic moments of lanthanides via single-electron bond and analyze magnetic properties of dimetallofullerenes with different lanthanides.

MA 33.6 Wed 16:15 H 1012

Electronic Configuration and Charge Transfer in Organometallic Ligand Complexes of Terbium (I, II, III) Ions — ●MARTIN TIMM¹, CHRISTINE BÜLOW¹, VICENTE ZAMUDIO-BAYER², REBECCA LINDBLAD³, BERND VON ISSENDORFF² und TOBIAS LAU¹ — ¹Helmholtz-Zentrum Berlin für Materialien und Energie, 12489 Berlin, Germany — ²Albert-Ludwigs-Universität Freiburg, 79098 Freiburg, Germany — ³Synkrotronljusfysik, Lunds Universitet, 22100 Lund, Sweden

Complexes of carbocyclic polyene ligands with lanthanoid atoms are of interest because of their large magnetic moments and magnetic anisotropy energy. In many of these complexes, there is a competition between charge transfer to the ligand in order to reach closed electronic shells according to Hückel's (4n + 2) rule, and the preference of lanthanoids to form +III oxidation states. We have, therefore, studied cationic mono- and di-ligated complexes of terbium atoms and cyclic C_nH_n ($n = 5, 6, 8$) molecules with preferential 0, -1, and -2 charge states by means of X-ray absorption and X-ray magnetic circular dichroism spectroscopy at the terbium $M_{4,5}$ edge. In all cases, we find the 4f⁸ configuration of terbium in its +III oxidation state. Furthermore, x-ray absorption spectra at the carbon K edge of the ligands indicate deviations from their planar ring structures, which is evidence of non-aromaticity.

15 min break

MA 33.7 Wed 16:45 H 1012

Effect of electron doping on Fe₄ single molecule magnets at surfaces — ●FABIAN PASCHKE, VIVIEN ENENKEL, PHILIPP ERLER, LUCA GRAGNANIELLO, and MIKHAIL FONIN — Fachbereich Physik, Universität Konstanz, 78457 Konstanz, Germany

The controlled deposition, characterization and manipulation of single molecule magnets (SMMs) on surfaces is one of the crucial topics for their use as units in future electronic and spintronic applica-

tions. We recently showed that by using the electropray deposition of Fe₄H SMMs self-organized arrays on insulating *h*-BN/Rh(111)¹ and graphene/Ir(111)² surfaces can be prepared. On graphene/Ir(111) the robustness of the Fe₄ complex is demonstrated as the magnetic anisotropy retains its bulk value despite a non-negligible electronic interaction with the substrate². Here we use scanning tunneling microscopy and spectroscopy as well as x-ray magnetic circular dichroism (XMCD) to investigate the effect of alkali metal (Li) doping on the charge state and magnetic anisotropy of Fe₄H on graphene/Ir(111) and Au(111). Doped molecules show emerging electronic states in the conduction gap and shifted energy positions of molecular orbitals. XMCD measurements indicate substantial changes in the multiplet structure at the Fe *L*-edge, presumably caused by partial reduction of Fe³⁺ to Fe²⁺ in the inorganic core. The magnetic anisotropy of the molecules is shown to be suppressed upon doping with alkali atoms.

[1] P. Erler et al., *Nano Lett.* 15, 4546 (2015). [2] L. Gragnaniello et al., *Nano Lett.*, 2017, in press.

MA 33.8 Wed 17:00 H 1012

Deposition and selective switching of a cationic Fe(III) compound on Au(111) and Cu₂N — ●MANUEL GRUBER¹, TORBEN JASPER-TÖNNIES¹, SUJOY KARAN², HANNE JACOB³, FELIX TUCZEK³, and RICHARD BERNDT¹ — ¹Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität Kiel — ²Institute of Experimental and Applied Physics, University of Regensburg — ³Institut für Anorganische Chemie, Christian-Albrechts-Universität Kiel

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. Investigations of single SCO molecules is challenging as the interaction with the substrate often leads to fragmentation or loss of functionality. So far, the focus was on Fe(II) based molecules, while SCO complexes with different metal ions (different oxidation states) would be desirable.

Using scanning tunneling microscopy, we evidence the first successful deposition of a cationic Fe(III) SCO complex, [Fe(pap)₂]⁺ (pap = N-2-pyridylmethylidene-2-hydroxyphenylaminato), on Au(111) and Cu₂N/Cu(100). The deposited Fe(III) SCO compound is controllably switched between three different states, each of them exhibiting a characteristic tunneling conductance. The conductance is therefore employed to readily read the state of the molecules [1,2].

This work was supported by SFB 677.

[1] Jasper-Toennies et al., *J. Phys. Chem. Lett.* 8, 1569 (2017)
[2] Jasper-Toennies et al., *Nano Lett.* 17, 6613 (2017)

MA 33.9 Wed 17:15 H 1012

X-ray magnetic spectroscopy study of switchable photomagnetic cages — ●NIÉLI DAFFÉ¹, MICHAL STUDNIAREK¹, JUAN-RAMÓN JIMÉNEZ², RODRIGUE LESCOUÉZEC², and JAN DREISER¹ — ¹Paul Scherrer Institut, 5232 Villigen PSI, Switzerland — ²Institut Parisien de Chimie Moléculaire, UPMC, F-75252 Paris, France

Molecules exhibiting switchable physical properties as a function of external stimuli have promising applications in molecule-based electronic devices. Therefore, the past decade has witnessed considerable interest in the design of new molecular systems with tunable functionalities. The most encouraging groups of compounds have emerged from the family of Prussian Blue Analogues (PBAs) that are known to exhibit concomitant changes in their magnetic and optical properties based on a metal-to-metal electron transfer when they are submitted to a temperature or light stimulus (D. Aguilà *et al.*, *Chem. Soc. Rev.* 45, 203-224, 2016). Molecular cages based on Co and Fe 3d transition ions linked by cyanide bridges are a prime example of a reversible conversion occurring between the diamagnetic (Fe^{II}_{LS}-CN-Co^{III}_{LS}) pairs and the

paramagnetic (Fe^{II}_{LS}-CN-Co^{III}_{HS}) ones (D. Garnier *et al.*, *Chem. Sci.* 7, 4825-4831, 2016). However, our understanding of the metal-to-metal charge transfer remains one of the key issues faced when studying PBAs, and it requires better insights on the geometry and the nature of the coordinated atoms. Using X-ray absorption spectroscopy and X-ray magnetic circular dichroism, we shed light onto the electronic and magnetic properties of the Co and Fe ions inside the CoFe photomagnetic cage upon temperature change and light irradiation.

MA 33.10 Wed 17:30 H 1012

Magnetite-gold Janus nanoparticles as all-in-one theranostics agents — ●MARIA V. EFREMOVA^{1,2}, YULIA A. NALENCH², VICTOR A. NAUMENKO², MAXIM A. ABAKUMOV³, MARINA SPASOVA⁴, MICHAEL FARLE⁴, ALEXANDER G. MAJOUGA^{1,2,5}, ULF WIEDWALD^{2,4}, and NATALIA L. KLYACHKO^{1,2} — ¹MSU, Moscow, Russia — ²NUST MISIS, Moscow, Russia — ³RNRMU, Moscow, Russia — ⁴UDE, Duisburg, Germany — ⁵MUCTR, Moscow, Russia

High-quality, 25 nm octahedral-shaped Fe₃O₄ magnetite nanocrystals are epitaxially grown on 9 nm Au seed nanoparticles (NPs) using a modified wet-chemical synthesis. Detailed studies of the structure and magnetism discover single-crystalline, nanosized Fe₃O₄ NPs with bulk-like magnetic properties (saturation magnetization of 86 Am²/kg at 300 K close to the bulk value of 92 Am²/kg and a Verwey transition from monoclinic to the cubic inverse spinel structure at T_V = 123 K). For MRI, these features lead to their high T₂-relaxivity in *in vitro* and *in vivo* experiments. We evaluate an at least doubled relaxivity as compared to the maximum values obtained for Fe₃O₄ – Au hybrids and a 3-5 times higher value as compared to commercial T₂ contrast agents in medical use. Moreover, first experiments on the magneto-mechanical action of the hybrid NPs in a low-frequency alternating magnetic field leads to a cell death rate of up to 44% compared to the control.

This work was supported by RFBR 17-54-33027 grant and Increase Competitiveness Programs of NUST MISIS K2-2016-069 (synthesis of nanomaterials) and K3-2017-022 (magnetic measurements).

MA 33.11 Wed 17:45 H 1012

Investigation of uptaking Aminosilane coated magnetite nanoparticles by cells — ●M. YOUHANNAYEE¹, S. NAKHAEIRAD², F. HAGHIGHI², R. AHMADIAN², A. SHAABAN³, J. NOTHACKER³, A. SCHMIDT³, A. BARBIAN⁴, K. KLAUKE⁵, C. JANI⁵, R. RABENALT⁶, P. ALBERS⁶, and M. GETZLAFF¹ — ¹angewandte physik, heinrich-heine universität, Düsseldorf — ²biochemie molekularbiologie II, HHU — ³Physikalische Chemie, Universität zu Köln — ⁴Anatomie I, HHU — ⁵bioanorganische Chemie, HHU — ⁶Klinik für Urologie, HHU

The basic principle of hyperthermia for cancer therapy arises from increasing the temperature of the specific organs and tissues from 41 °C to 46 °C [1]. Using magnetic nanoparticles and applying alternating magnetic field (AC) on them is so called as magnetic fluid hyperthermia. In this project superparamagnetic iron oxide nanoparticles (SPION) with functionalized surface Aminosilane around the iron oxide core are applied which have been widely using in different experimental applications *in vivo* and *in vitro* experiments because of biocompatibility and low toxicity of these particles. In order to characterize the morphological properties of SPION variety of measurements and evaluations were carried out such as transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR). Additionally the effect of AC magnetic field on particles was observed. To investigate the effect of magnetic nanoparticles on cells and their uptaking by cells TEM, MTT measurement and flow cytometry (FACS) were carried out. [1] A. Jordan, R. Scholz, P. Wust, H. Fähling, R. Felix. *JMMM* 201 (1999): 413-419.