

MA 33: Bio- Molecular Magnetism

Time: Thursday 10:15–12:45

Location: HSZ 103

MA 33.1 Thu 10:15 HSZ 103

Mn₁₂ Single-Molecule Magnets on Surfaces: Achievements and Perspectives — ●SÖNKE VOSS¹, MICHAEL BURGERT², MIKHAIL FONIN¹, ULRICH GROTH², and ULRICH RÜDIGER¹ — ¹Fachbereich Physik, Universität Konstanz, 78457 Konstanz — ²Fachbereich Chemie, Universität Konstanz, 78457 Konstanz

During the past years, a variety of studies on the structural, electronic as well as magnetic properties of Mn₁₂ single-molecule magnets (SMMs) deposited on surfaces have been performed. Recent investigations on molecular monolayers indicated the absence of all the fascinating magnetic properties known from SMM single crystals, like hysteresis of purely molecular origin or the ability to directly observe quantum tunnelling of magnetization. Nevertheless, results obtained by means of advanced characterization techniques indicated that fundamental structural as well as electronic properties of individual Mn₁₂ molecules are preserved after the deposition on a surface.

We will present the most recent achievements in the characterization of Mn₁₂ monolayers by means of scanning probe techniques, synchrotron radiation, and magnetization measurements. Potential reasons for the lack of a magnetic hysteresis in the monolayers will be discussed. Furthermore, advanced approaches towards an ultimate clarification of the suitability of Mn₁₂ SMMs for studies on molecule-based spintronic devices will be described.

MA 33.2 Thu 10:30 HSZ 103

Magnetic properties of planar TM-Ni binuclear single molecular magnets — ●ULF WIEDWALD¹, FLORIAN MÖGELE², BERNHARD RIEGER³, and PAUL ZIEMANN¹ — ¹Institut für Festkörperphysik, Universität Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany — ²Institut für Materialien und Katalyse, Universität Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany — ³WACKER-Lehrstuhl für Makromolekulare Chemie, Technische Universität München, Lichtenbergstraße 4, 85747 Garching bei München

Single molecular magnets are fascinating because of various possible coupling schemes between magnetic sites and resulting differences of the total magnetic moment, magnetic anisotropy and ordering temperature. Planar TM-Ni metallo-organic molecules (TM=V, Mn, Fe, Co, Ni, Cu) are synthesized each consisting of two magnetic sites and two identical alkyl chains forming a V-shape molecule. Dried powders are investigated by SQUID magnetometry. We find a resulting magnetization ranging from 0.2 μ_B /molecule for V-Ni molecules to 1.7 μ_B /molecule for Co-Ni molecules at B = 5.5 T and T = 2 K. Temperature-dependent susceptibility measurements suggest antiferromagnetic coupling of the two magnetic sites at T = 2 K while at higher temperature a transition to ferromagnetic coupling is likely. The ordering temperatures are found between 9 and 34 K for Ni-Ni and Mn-Ni molecules, respectively.

MA 33.3 Thu 10:45 HSZ 103

magnetic excitations and spin correlations in the spherical keplerate molecular magnet {Mo72Fe30} — ●ZHENDONG FU¹, PAUL KÖGERLER^{1,2}, ULRICH RÜCKER¹, and THOMAS BRÜCKEL¹ — ¹Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany — ²Institut für Anorganische Chemie, RWTH Aachen, D-52074 Aachen, Germany

As one of the biggest molecular magnets that have been synthesized, the polyoxomolybdate {Mo72Fe30} allows us to investigate a highly symmetric and frustrated spin structure and provides us an ideal test-bed for the theory on frustrated quantum spin systems. In our work, the low-field magnetic susceptibility measurement yields a Curie temperature about -20 K, indicating weak antiferromagnetic exchange interactions between the nearest neighbors. The low lying magnetic excitations of {Mo72Fe30} are characterized in terms of field-dependent heat capacity and inelastic neutron scattering measurements. The energy gaps resolved from the experimental data are located at about 0.1 and 0.7 meV, consistent with the quantum rotational band model for {Mo72Fe30} system [1]. The diffuse neutron scattering study with polarization analysis on {Mo72Fe30} polycrystals reveals characteristic spin correlations close to a coplanar three-sublattice ground state. Our observations agree with the previous theoretical model for this system, but also suggest that refinements should be done to the existing theoretical models. [1] J. Schnack, M. Luban and R. Modler,

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MA 33.4 Thu 11:00 HSZ 103

Symmetry assisted approximate diagonalization of antiferromagnetic molecules — ●ROMAN SCHNALLE¹ and JÜRGEN SCHNACK² — ¹Universität Osnabrück, Fachbereich Physik, D-49069 Osnabrück — ²Universität Bielefeld, Fakultät für Physik, Postfach 100131, D-33501 Bielefeld

The spectrum of many interesting molecular antiferromagnets is theoretically often inaccessible due to the prohibitive size of the underlying Hilbert space. Experimentally the system of interest might very well be accessible for instance by neutron scattering, EPR, specific heat or magnetization measurements. The interpretation of the experimental data thus suffers from numerical restrictions.

In order to get insight into the low-temperature behaviour of large spin systems describing magnetic molecules - either bipartite or frustrated - we develop an approximate diagonalization. This theory rests on the observation that the low-lying spectrum of many finite size antiferromagnets can be rather successfully approximated by so-called rotational bands [1], which are the eigenstates of the rotational band Hamiltonian. We use an increasing number of these basis states (bands) for an approximate diagonalization of the full Heisenberg Hamiltonian [2]. Additionally point-group symmetries are used for a further reduction of the dimensionalities of the occurring matrices and a specific labelling of the eigenstates.

[1] J. Schnack, M. Luban, Phys. Rev. B **63**, 014418 (2000).[2] O. Waldmann, Phys. Rev. B **75**, 012415 (2007).

MA 33.5 Thu 11:15 HSZ 103

Complete diagonalization studies of anisotropic magnetic molecules — ●JUERGEN SCHNACK — Universität Bielefeld, Fakultät für Physik, Postfach 100131, D-33501 Bielefeld

Thanks to recent progress both on the level of computer resources as well as on the level of theoretical modeling it is nowadays possible to discuss the behavior of anisotropic magnetic molecules in the context of a full spin Hamiltonian. This goes far beyond the giant spin Hamiltonian approach and offers the opportunity to investigate for instance effects of more than the ground state multiplet. We will comment on these recent developments and discuss two specific molecules in detail which possess the magnetic cores Mn₆Fe and Mn₃Cr.

[1] T. Glaser, J. Schnack *et al.*, Inorg. Chem. (2008) in press

MA 33.6 Thu 11:30 HSZ 103

Can the Hubbard model explain the steps observed in the magnetization curve of {Ni₄Mo₁₂}? — ●MARTIN HÖCK and JÜRGEN SCHNACK — Universität Bielefeld, Fakultät für Physik, Postfach 100131, D-33501 Bielefeld

The low-temperature magnetization curve of the magnetic molecule {Ni₄Mo₁₂} features four nonequidistant steps which cannot be explained using a Heisenberg model [1]. In his article [2], V. Kostyuchenko presents a spin-1 model with biquadratic and three-spin interactions and claims that it is the strong coupling limit of a certain Hubbard model. This spin-1 model correctly predicts the position of the steps in the magnetization curve.

We investigate whether the Hubbard model proposed in [2] is really capable of describing {Ni₄Mo₁₂}. To this end, we calculate its eigenvalues using numerical exact diagonalization and try to fit its parameters to the experimental magnetization data. We are unable to find suitable fit parameters although the parameter space of the model is only two-dimensional.

Therefore, we analyze the strong coupling limit of the Hubbard model and rederive its effective spin model up to order $\mathcal{O}(U^{-3})$. The spin Hamiltonian which we obtain differs from the one presented by Kostyuchenko. We arrive at the final conclusion that the Hubbard model as proposed in [2] is not suited to describe the molecule {Ni₄Mo₁₂}.

[1] J. Schnack *et al.*, Phys. Rev. B **73**, 094401 (2006);[2] V. V. Kostyuchenko, Phys. Rev. B **76**, 212404 (2007)

MA 33.7 Thu 11:45 HSZ 103

SMM-like magnetic properties of Cobalt(II) Cubane

[Co₄(HL)₄(Cl)₄] — •KLAUS GIEB¹, KONSTANTIN PETUKHOV¹, ANDREAS SCHEURER², AYUK M. AKO², ROLF W. SAALFRANK², and PAUL MÜLLER¹ — ¹Department für Physik, Universität Erlangen-Nürnberg, Germany — ²Department für Chemie und Pharmazie, Universität Erlangen-Nürnberg, Germany

We report on magnetic properties of the novel tetranuclear cobalt compound [Co₄(HL)₄(Cl)₄]. We have found that this Co(II) cubane system shows evident single-molecule magnet (SMM)-like behavior. In particular, we have found that the nominal ground spin state of this complex is S = 6. The uniaxial anisotropy parameter D has a negative value of around -1.6 Kelvin. Relaxation studies have evidenced a single relaxation process following an Arrhenius law. The anisotropy barrier is $\Delta \approx 55.8$ K and the relaxation time is $\tau_0 \approx 10^{-8}$ s. The measurements were performed by means of SQUID magnetometry, AC susceptibility measurements, and micro-Hall-probe hysteretic characterization.

MA 33.8 Thu 12:00 HSZ 103

Anisotropy and frustration of the high-spin

[Cr^{III}Mn^{II}₃(PyA)₆Cl₃] molecule — •MANUEL PRINZ¹, MICHAEL RAEKERS¹, KARSTEN KUEPPER², MARC UHLARZ², SUMIT KHANRA³, BIPLAB BISWAS³, THOMAS WEYHERMÜLLER³, JÜRGEN SCHNACK⁴, and MANFRED NEUMANN¹ — ¹University of Osnabrück, Fachbereich Physik, D-49069 Osnabrück — ²Forschungszentrum Dresden-Rossendorf, POB 51 01 19, D-01314 Dresden — ³MPI für Bioanorganische Chemie, D-45470 Mülheim an der Ruhr — ⁴Universität Bielefeld, Fakultät für Physik, D-33501 Bielefeld

Molecular magnets incorporate transition metal ions with organic groups providing a bridge to mediate magnetic exchange interactions between the ions. There are star-shaped molecules in which antiferromagnetic couplings between the central and peripheral atoms is predominantly present. Those configurations lead to an appreciable spin moment in the non-frustrated ground state. In spite of its topologically simple magnetic system, the [Cr^{III}Mn^{II}₃(PyA)₆Cl₃] (**CrMn₃**) molecule exhibits non-trivial magnetic properties, like anisotropy and frustration. In the present work we elucidate the underlying magnetic properties of the hetero nuclear, spin-frustrated **CrMn₃** molecule applying high magnetic field measurements, X-ray magnetic circular dichroism (XMCD), anisotropic Heisenberg simulations and classical spin dynamic methods. Modeling the high field data by anisotropic Heisenberg simulations and discussion of the various spin Hamiltonian parameters leads to a validation of our element selective transition metal XMCD spin moments at a magnetic field of 5 T and a temperature of 5 K.

MA 33.9 Thu 12:15 HSZ 103

Effects of the Ligand Shell on the Single-Molecule Magnet

Behavior in Co₅ Clusters — •J. NEHRKORN¹, O. WALDMANN¹, F. KLÖWER², Y. H. LAN², and A. K. POWELL² — ¹Physikalisches Institut, Universität Freiburg, D-79104 Freiburg, Germany — ²Institut für Anorganische Chemie, Universität Karlsruhe, D-76128 Karlsruhe, Germany

Enhancing single-molecule magnet (SMM) behavior in molecular nanomagnets to higher temperatures is one of the great aims in this field. Incorporating Co^{II} ions, because of their high magnetic anisotropy, has recently attracted much interest. In this work we study three Co₅ clusters which exhibit similar cores, but differ in their coordination spheres due to the use of different ligands. Our dc and ac magnetic data revealed that one compound is clearly a SMM, one is a weak SMM, and the third one is no SMM. We interpret the data on the basis of an effective-spin Hamiltonian, which reproduces the magnetic data well and allows us to understand the trend of SMM behavior. A subtle effect of highly anisotropic systems was observed: anisotropic ferromagnetic couplings together with highly anisotropic **g** matrices can yield susceptibility curves with a temperature dependence usually associated to antiferromagnetic interactions.

MA 33.10 Thu 12:30 HSZ 103

Controlling the magnetic coupling of Fe-porphyrin molecules

to ferromagnetic films: a temperature-dependent XMCD investigation — •MATTHIAS BERNIEN¹, JORGE MIGUEL¹, CLAUDIA WEIS², MARTEN PIANTEK¹, XIAOYING XU¹, PHILIPP ECKHOLD¹, JULIA KURDE¹, KLAUS BABERSCHKE¹, WOLFGANG KUCH¹, and HEIKO WENDE² — ¹Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin — ²Fachbereich Physik, Experimentalphysik - AG Wende and Center for Nanointegration (CeNIDE), Universität Duisburg-Essen, Lotharstrasse 1, D-47048 Duisburg

Metal complexes on surfaces are the topic of intensive scientific investigations, since the properties of their central ion, determined by the adjacent ligands, can be widely tuned by the chemical design of the molecule. When paramagnetic porphyrin molecules are deposited onto ferromagnetic substrates, the spin of the metal center aligns parallel to the magnetization of the substrate. Tuning the molecule-substrate interaction would be an important step towards the realization of a surface-mounted molecular spintronic device. Here we have realized different magnetization directions and coupling strengths by choice of the substrate. We have determined the coupling strength between submonolayers of Fe octaethylporphyrins and ferromagnetic substrates by detailed temperature-dependent X-ray magnetic circular dichroism measurements. The vision of tailoring the magnetic coupling between the porphyrin molecules and the ferromagnetic substrates will be discussed.

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