

## MA 27: Bio- and Molecular Magnetism

Time: Thursday 14:30–18:00

Location: EB 202

MA 27.1 Thu 14:30 EB 202

**Can large magnetic anisotropy and high spin really coexist?** — ELISEO RUIZ<sup>1</sup>, JORDI CIRERA<sup>1</sup>, JOAN CANO<sup>1,2</sup>, SANTIAGO ALVAREZ<sup>1</sup>, ●CLAUDIA LOOSE<sup>3</sup>, and JENS KORTUS<sup>3</sup> — <sup>1</sup>Departament de Química Inorgánica and Institut de Recerca de Química Teórica i Computacional, Universitat de Barcelona, Diagonal 647,08028 Barcelona, Spain — <sup>2</sup>Institució Catalana de Recerca i Estudis Avançats, Spain — <sup>3</sup>Institut für Theoretische Physik, TU Bergakademie Freiberg, Leipziger Str. 23, D-09599 Freiberg, Germany

This theoretical study discusses the interplay of the magnetic anisotropy and magnetic exchange interaction of two Mn<sub>6</sub> complexes. Our results for two polynuclear Mn<sub>6</sub> complexes show a very strong dependence of the D value on the spin of the ground state while the energy barriers are practically constant. Thus, complex 2 with a large spin ( $S = 12$ ) favoured by ferromagnetic interactions has a small D value, while the lower spin complex 1 ( $S = 4$ ) has a large D value. Therefore we suggest, that a large magnetic anisotropy is not favoured by a high spin state of the ground state.

MA 27.2 Thu 14:45 EB 202

**Inelastic neutron scattering on an antiferromagnetic tetrahedral Ni<sub>4</sub> molecule** — ●JOSCHA NEHRKORN<sup>1</sup>, OLIVER WALDMANN<sup>1</sup>, and HANNU MUTKA<sup>2</sup> — <sup>1</sup>Physikalisches Institut, Universität Freiburg, D-79104 Freiburg, Germany — <sup>2</sup>Institut Laue Langevin, BP 156-38042, Grenoble Cedex 9, France

We study the magnetic excitations in a tetrahedral Ni<sub>4</sub> molecule by inelastic neutron scattering (INS). The Ni<sub>4</sub> cluster consists of four antiferromagnetically coupled spin-1 Ni<sup>2+</sup> ions in an almost perfect tetrahedral arrangement. The antiferromagnetic Heisenberg coupling should lead to a  $S = 0$  ground state with higher-lying  $S = 1$  and  $S = 2$  levels. In our INS measurements we see peaks at transition energies in accord with the Heisenberg spectrum, but which violate the INS selection rule  $\Delta S = 0, \pm 1$ . That is, we observe not only the peaks which would correspond to the  $S = 0 \rightarrow S = 1$  and  $S = 1 \rightarrow S = 2$  transitions, but also a peak which would have to be assigned as a  $S = 0 \rightarrow S = 2$  transition. However, Ni<sup>2+</sup> ions are known to exhibit single-ion anisotropies as large as several 10 K, which hence, apparently, should not be neglected. Therefore, the effects of a single-ion anisotropy in a tetrahedral symmetry on the INS spectrum is explored by exact numerical calculations.

MA 27.3 Thu 15:00 EB 202

**Multiple nearest-neighbor exchange constants in the frustrated magnetic molecules {Mo<sub>72</sub>Fe<sub>30</sub>} and {Mo<sub>72</sub>Cr<sub>30</sub>}** — ●CHRISTIAN SCHRÖDER<sup>1,2</sup>, RUSLAN PROZAROV<sup>2</sup>, HIROYUKI NOJIRI<sup>3</sup>, and MARSHALL LUBAN<sup>2</sup> — <sup>1</sup>University of Applied Sciences, Bielefeld, Germany — <sup>2</sup>Ames Laboratory & Iowa State University, Ames, Iowa, USA — <sup>3</sup>Tohoku University, Sendai, Japan

Our measurements of the differential susceptibility  $\partial M/\partial H$  of the frustrated Keplerate magnetic molecules {Mo<sub>72</sub>Fe<sub>30</sub>} and {Mo<sub>72</sub>Cr<sub>30</sub>} reveal a pronounced dependence on magnetic field ( $H$ ) and temperature ( $T$ ) in the low  $H$  – low  $T$  regime, contrary to the predictions of existing models. Excellent agreement with experiment is achieved upon formulating a nearest-neighbor classical Heisenberg model where the 60 nearest-neighbor exchange interactions in each molecule, rather than being identical as has been assumed heretofore, are described by a two-parameter probability distribution of values of the exchange constant. We suggest that the probability distribution provides a convenient theoretical platform for summarizing the combined effects of multiple microscopic mechanisms that disrupt the idealized picture of a Heisenberg model based on a single value of the nearest-neighbor exchange constant.

MA 27.4 Thu 15:15 EB 202

**Pulsed W-Band ESR studies on Cr<sub>7</sub>Ni** — ●CHRISTOPH SCHLEGEL<sup>1</sup>, JORIS VAN SLAGEREN<sup>1,2</sup>, HANS-JÜRGEN KÜMMERER<sup>3</sup>, GERT DENNINGER<sup>3</sup>, RICHARD E. P. WINPENNY<sup>4</sup>, and MARTIN DRESSEL<sup>1</sup> — <sup>1</sup>Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany — <sup>2</sup>School of Chemistry, University of Nottingham, Nottingham NG7 2RD, United Kingdom — <sup>3</sup>Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany — <sup>4</sup>Department of Chemistry, University

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For quantum information processing sufficiently long coherence times of the employed system are necessary. Molecular magnets are potential systems for the realization of quantum bits. Both spin-lattice and spin-spin relaxation times of Cr<sub>7</sub>NiF<sub>8</sub>Piv<sub>16</sub> were measured with a pulsed W-Band spectrometer. The measurements were performed on diluted frozen solutions, because in Cr<sub>7</sub>Ni crystals dipolar interactions lead to very short coherence times. At 5 K and a concentration of 0.2 mg/ml, T<sub>1</sub> was determined to be 2300 ns, while T<sub>2</sub> was measured to be 357 ns, which is comparable to literature values. [1] To improve the coherence times, it is necessary to understand the decoherence mechanism. One of the decoherence pathways is through coupling with the nuclear spins. With pulsed ENDOR the hyperfine coupling of the electron spin to the nuclear spin of the protons could be quantified to -0.8 MHz in a 1 mg/ml solution. Surprisingly, no coupling to the nuclear spin of fluorine could be found.

[1] A. Ardavan et al., Phys. Rev. Lett. **98**, 057201 (2007)

MA 27.5 Thu 15:30 EB 202

**High-frequency ESR and frequency domain magnetic resonance spectroscopic studies of single molecule magnets in frozen solution** — ●FADI EL HALLAK<sup>1</sup>, JORIS VAN SLAGEREN<sup>1</sup>, MARTIN DRESSEL<sup>1</sup>, JORDI GÓMEZ-SEGURA<sup>2</sup>, and DANIEL RUIZ-MOLINA<sup>2</sup> — <sup>1</sup>Physikalisches Institut, Universität Stuttgart, Stuttgart, Germany — <sup>2</sup>Institut de Ciència de Materials de Barcelona, Bellaterra, Spain

Frozen solutions of the single molecule magnet Mn<sub>12</sub>-Pivalate (or trimethylacetate) are studied by magnetization and magnetic resonance investigations. AC magnetic susceptibility measurements show that the system is stable in solution. Interestingly, the barrier and prefactor for the thermally activated magnetization relaxation are the same as in the solid state. This means that this system is not influenced by its surroundings, in contrast to other Mn<sub>12</sub> derivatives. The zero-field-splitting spin Hamiltonian parameters of Mn<sub>12</sub>Piv in solution are determined by magnetic resonance spectroscopy methods to be very similar to those in the solid state. By these methods, it is also possible to distinguish between truly dissolved and precipitated species, which is not possible by magnetization measurements.

MA 27.6 Thu 15:45 EB 202

**Electronic Spin Dynamics and Static Order in Coupled Magnetic Keplerates Fe<sub>30</sub>Mo<sub>72</sub>** — ●F.J. LITTERST<sup>1</sup>, H.-H. KLAUSS<sup>1,2</sup>, T. DELLMAN<sup>1,2</sup>, J. SCHNACK<sup>3</sup>, R. KLINGELER<sup>4</sup>, and A. MÜLLER<sup>5</sup> — <sup>1</sup>IPKM, TU Braunschweig, Mendelssohnstr. 3, 38106 Braunschweig — <sup>2</sup>IFP, TU Dresden, Zellesche Weg 16, 01069 Dresden — <sup>3</sup>Fakultät für Physik, Univ. Bielefeld, 33501 Bielefeld — <sup>4</sup>IFW-Dresden, Helmholtzstr. 20, 01171 Dresden — <sup>5</sup>Anorganische Chemie I, Univ. Bielefeld, 33501 Bielefeld

In the polyoxomolybdate nanomolecule Fe<sub>30</sub>Mo<sub>72</sub> 30 S=5/2 FeIII ions are located on the vertices of an icosidodecahedron coupled via nearest-neighbor antiferromagnetic interactions J [1]. In the paramagnetic molecules the electronic ground state and excitations are governed by the strong magnetic frustration on the Kagomé-like surface [2]. A modified system with much stronger inter-molecular exchange interaction [3] shows several anomalies in the magnetic susceptibility below 5 K.

We performed <sup>57</sup>Fe-Mössbauer spectroscopy on the isolated and magnetically interacting molecules. Around 4.45 K (broad maximum in  $\chi(T)$ ) dynamic magnetic hyperfine spectra with magnetically inequivalent sites appear. Around 2.45 K a drop in  $\chi(T)$  is accompanied by a slowing down of hyperfine dynamics and indicates antiferromagnetic order.

[1] A. Müller et al., Angew. Chem. Int. Ed. Engl. **38** (1999) 3238. [2] V.O. Garlea et al., Phys. Rev. B **73** (2006) 024414. [3] A. Müller et al., Angew. Chem. Int. Ed. Engl. **39** (2000) 1612.

MA 27.7 Thu 16:00 EB 202

**Broadband electron paramagnetic resonance of single-molecule magnets at millikelvin temperatures.** — ●KONSTANTIN PETUKHOV<sup>1</sup>, KLAUS GIEB<sup>1</sup>, THORSTEN GLASER<sup>2</sup>, WOLFGANG HANSEN<sup>3</sup>, and PAUL MÜLLER<sup>1</sup> — <sup>1</sup>Institut für Physik der Kondensierten Materie, Universität Erlangen-Nürnberg — <sup>2</sup>Lehrstuhl für Anorganische Chemie I, Universität Bielefeld — <sup>3</sup>Institut für Angewandte Physik, Universität Hamburg

We present a technique which combines Hall-bar magnetometry of single-molecule magnets (SMMs) with broadband microwave absorption measurements. This electron paramagnetic resonance-like spectroscopy can be performed at millikelvin temperatures and enables the use of short-pulsed microwave radiation. Thus, the spin dynamics of SMMs can be studied. We present measurements on novel  $Mn_6Mn$  and  $Mn_6Cr$  single-molecule magnets.

MA 27.8 Thu 16:15 EB 202

**Spin-dynamics of ferric wheels in high magnetic fields** — ●LARS SCHNELZER and BERND PILAWA — Physikalisches Institut, Universität Karlsruhe (TH), D-76131 Karlsruhe

The dynamic properties of the antiferromagnetic cyclic hexanuclear iron(III) complexes  $^{23}Na/^{7}Li@Fe_6(tea)_6$  have been studied by means of nuclear magnetic resonance. We analyzed the longitudinal relaxation rate  $T_1^{-1}$  of the central alkali ions  $^{23}Na$  and  $^{7}Li$  in the magnetic field range up to 20 T at a temperature of 2 K. The  $T_1^{-1}$  measurements reveal the influence of the levelcrossing between the  $S=0$  and  $S=1$  states by an enhanced relaxation rate, as well as a strong decrease of the relaxation rate at characteristic fields between level crossings. In comparison with the calculated fluctuation spectrum of the electronic spins this suppression of the  $T_1$ -rate indicates an extremely reduced line width of the electronic resonance around  $\omega=0$  (the so called  $\omega_0$ -resonance).

MA 27.9 Thu 16:30 EB 202

**Coordination geometry induced changes on magnetic parameters of Cu(II) complexes** — ●BJÖRN BRÄUER<sup>1</sup>, TOBIAS RÜFFER<sup>1</sup>, DANTE GATTESCHI<sup>2</sup>, MARIA FITTIPALDI<sup>2</sup>, ANDREA CANESCHI<sup>2</sup>, FLORIAN WEIGEND<sup>3</sup>, and GEORGETA SALVAN<sup>1</sup> — <sup>1</sup>Chemnitz University of Technology, Department of Physics, Reichenhainer Straße 70, D-09126 Chemnitz — <sup>2</sup>University of Florence, Department of Chemistry, Via della Lastruccia 3, I-50019 Florence — <sup>3</sup>Forschungszentrum Karlsruhe, Institute for Nanotechnology, Postfach 3640, D-76021 Karlsruhe

Cu(II)-bis(oxamato) complexes are prominent representatives for basic research studies of magnetic exchange phenomena [1]. We have used Electron Paramagnetic Resonance (EPR) spectroscopy to study the dependence of the hyperfine coupling constants  $A$  and the spin density distribution on the structural parameters of mono-nuclear complexes. Furthermore, the influence of such variations on the super exchange coupling parameter  $J$  of the respective tri-nuclear complexes was investigated. It was shown that deviations from the square planar coordination geometry decrease the delocalisation of spins leading to a smaller  $J$  value, i. e. a smaller antiferromagnetic interaction. The obtained parameters were also calculated by means of Density Functional Theory (DFT). The  $J$  parameters were determined using the broken symmetry approach and the influence of packing effects, counter ions, and bridging ligands were investigated. The CONductor like Screening Field MOdel (COSMO) was found to be a suitable model for reliable predictions of experimental trends. [1] O. Kahn, Molecular Magnetism, VCH Weinheim, 1993.

MA 27.10 Thu 16:45 EB 202

**Enhanced magnetocaloric effect in frustrated magnetic molecules with icosahedral symmetry** — ●JÜRGEN SCHNACK<sup>1</sup> and JOHANNES RICHTER<sup>2</sup> — <sup>1</sup>Universität Bielefeld, Fakultät für Physik, PF 100131, D-33501 Bielefeld — <sup>2</sup>Universität Magdeburg, Institut für Theoretische Physik, PF 4120, D-39016 Magdeburg

We investigate the magnetocaloric properties of certain antiferromagnetic spin systems that have already been or very likely can be synthesized as magnetic molecules. It turns out that the special geometric frustration which is present in antiferromagnets that consist of corner-sharing triangles leads to an enhanced magnetocaloric effect with high cooling rates in the vicinity of the saturation field. These findings are compared with the behavior of a simple unfrustrated spin ring as well as with the properties of the icosahedron. To our surprise, also for the icosahedron large cooling rates can be achieved but due to a different kind of geometric frustration. [J. Schnack, R. Schmidt, J. Richter, Phys. Rev. B **76** (2007) 054413]

MA 27.11 Thu 17:00 EB 202

**Electronic structure of phthalocyanines** — ●PREDRAG LAZIC, NICOLAE ATODIRESEI, and STEFAN BLÜGEL — Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

The coupling between the  $\pi$ -delocalized electrons of the phthalocyanine with the  $d$ -localized electrons of a metal yields to a class of

organometallic molecules with interesting physical properties. We have performed the *ab-initio* calculations on the gas phase of metal-phthalocyanine molecules as well as their adsorption on a Cu(111) surface precovered with a monolayer of sodium chloride. In order to describe accurately the molecule-substrate interaction we have used the seamless approach to include the long range correlation effects (i.e. van der Waals interaction) which are not properly described in the present DFT codes using LDA or GGA exchange-correlation functionals.

MA 27.12 Thu 17:15 EB 202

**Approximate spectra for magnetic molecules with sublattice structure** — ●ROMAN SCHNALLE<sup>1</sup> and JÜRGEN SCHNACK<sup>2</sup> — <sup>1</sup>Universität Osnabrück, Fachbereich Physik, D-49069 Osnabrück — <sup>2</sup>Universität Bielefeld, Fakultät für Physik, PF 100131, D-33501 Bielefeld

A lot of interesting magnetic molecules cannot be treated with numerically exact diagonalization routines because of the huge dimensions of the Hilbert spaces. Therefore approximate numerical techniques are highly desirable to obtain information about the energy spectra of the investigated systems. In a recent work we developed a perturbation theory that is guided by an approximate Hamiltonian for spin systems with sublattice structure, the rotational band Hamiltonian [1]. Within this perturbative approach an increasing number of states is taken into account. These states are chosen to be those with low-lying energies in the spectrum of the rotational band Hamiltonian [2].

[1] J. Schnack, M. Luban, Phys. Rev. B **63**, 014418 (2000)

[2] O. Waldmann, Phys. Rev. B **75**, 012415 (2007)

MA 27.13 Thu 17:30 EB 202

**Electronic and Magnetic Properties of Mn<sub>12</sub> Single-Molecule Magnets on the Au(111) Surface** — ●SÖNKE VOSS<sup>1</sup>, MICHAEL BURGERT<sup>1</sup>, MIKHAIL FONIN<sup>1</sup>, CHRISTIAN MICHAELIS<sup>2</sup>, IVAN BRIHUEGA<sup>2</sup>, YURY S. DEDKOV<sup>3</sup>, ULRICH GROTH<sup>1</sup>, KLAUS KERN<sup>2</sup>, and ULRICH RÜDIGER<sup>1</sup> — <sup>1</sup>Universität Konstanz, 78457 Konstanz — <sup>2</sup>Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart — <sup>3</sup>Institut für Festkörperphysik, Technische Universität Dresden, 01062 Dresden

The paramount interest in single-molecule magnets (SMMs) like  $Mn_{12}$ -acetate and its derivatives was inspired by numerous experimental and theoretical insights indicating the feasibility of addressing quantum effects of magnetism on a molecular scale. Due to its relatively high blocking temperature ( $\sim 3K$ ) combined with the ability to identify well-defined spin states,  $Mn_{12}$  still remains the most favoured SMM possibly allowing the detection of magnetic fingerprints in transport properties of a single molecule.

In this work, the electronic properties of  $Mn_{12}$  molecules chemically grafted on Au(111) surfaces have been studied by means of low temperature as well as room temperature scanning tunneling microscopy and spectroscopy (STS), x-ray absorption spectroscopy and photoelectron spectroscopy. The results revealed signatures from most probably intact  $Mn_{12}$  molecules while STS measurements in magnetic fields indicate the possibility to identify magnetic fingerprints in scanning tunneling spectra. The results will be discussed with respect to previous attempts to perform transport measurements on  $Mn_{12}$  SMMs.

MA 27.14 Thu 17:45 EB 202

**Fe-porphyrin monolayers on ferromagnetic substrates: Electronic structure and magnetic coupling strength** — ●MATTHIAS BERNIEN<sup>1</sup>, XIAOYING XU<sup>1</sup>, JORGE MIGUEL<sup>1</sup>, MARTEN PIANTEK<sup>1</sup>, PHILIPP ECKHOLD<sup>1</sup>, JUN LUO<sup>1</sup>, JULIA KURDE<sup>1</sup>, KLAUS BABERSCHKE<sup>1</sup>, WOLFGANG KUCH<sup>1</sup>, HEIKO WENDE<sup>2</sup>, and PANKAJ SRIVASTAVA<sup>2</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany — <sup>2</sup>Fachbereich Physik, Experimentalphysik - AG Wende, Universität Duisburg-Essen, Lotharstrasse 1, D-47048 Duisburg, Germany

Paramagnetic Fe-porphyrin molecules are promising candidates for applications in molecular nano-electronics. A fundamental understanding of the interaction of these molecules with ferromagnetic substrates is essential to realize future functional devices. Here we present systematic x-ray absorption and x-ray magnetic circular dichroism (XMCD) studies on octaethylporphyrin-Fe(III) chloride molecules sublimated onto epitaxially grown Ni and Co films on Cu(100). The fine structures observed in the absorption and dichroic spectra of the Fe-L<sub>2,3</sub> edges are explained in terms of different Fe  $3d$  orbitals probed in angular-dependent measurements. The coverage of Fe-porphyrin molecules is varied from submonolayer to 1.5 monolayer, and measurements were

carried out at room as well as at low temperatures. From the temperature dependence of the Fe-XMCD signal, a weaker coupling strength

between the Fe atom and the Ni substrate is found as compared to the Co case.