High-resolution NEXAFS and XMCD investigations of magnetic supramolecules

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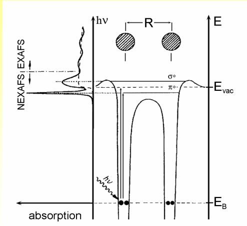
Introduction

We have investigated the electronic structure of supramolecular clusters with NEXAFS spectroscopy. For laterally resolved spectra, advantage was taken of scanning transmission x-ray microscopes (STXM) at ALS, Berkeley. To gain information about the internal magnetic properties of these aggregates, investigations utilizing the x-ray magnetic circular dichroism (XMCD) technique were carried out at BESSY, Berlin. Additionally, time-dependent studies on the effect of radiation damage were conducted at both facilities.

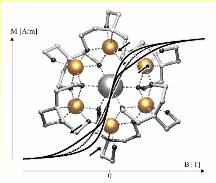
The studied supramolecules all contain several octahedrally coordinated paramagnetic transition-metal ions (Mn, Fe). These show strong NEXAFS resonances at the $L_{2,3}$ edges which are sensitive to minor chemical changes and give rise to strong dichroism. The metal ions and the bridging oxygen atoms build up an antiferromagnetically coupled network with all metal ions in a single plane. The electronic and magnetic properties of the molecule should be fine-tunable by changes to the ligands through chemical synthesis.

NEXAFS

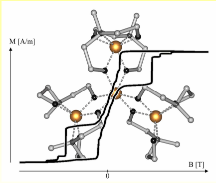
NEXAFS (near-edge x-ray absorption fine structure) probes the **unoccupied electronic states.** By tuning the x-ray energy to the absorption edge of the respective element (only possible with a tunable x-ray source), the coupling of the local excitation to the electronic system of the molecule is detected. This study is focused on the L-edge excitation of the metal atoms, which are more sensitive to changes of their valence state.



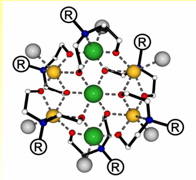
Our model substances (Synthesis: AK Saalfrank, OC Univ. ER[1,2])



Na⊂$Fe^{III}_6(L^1)_6Cl$
„ferric wheel“
S = 0



Fe^{III}⊂$[Fe^{III}(L^2)_2]_3$
„ferric star“
S = 10/2[3]



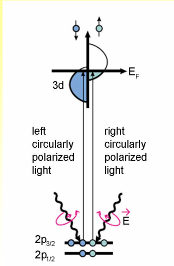
Mn^{II}⊂$[Mn^{II}_2Mn^{III}_4Cl_6(L^3)_6]$
„manganese wheel“
? S = 31/2 ? S = 20/2 ?

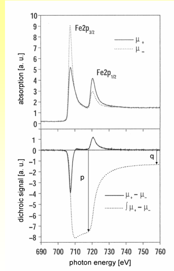
XMCD[7]

XMCD (x-ray magnetic circular dichroism) uses circularly polarized light and a strong magnetic field to achieve spin-polarized NEXAFS data.

Dependent on the polarization of the incident light, electrons are excited into either majority or minority spin states, by which the density of these spin states is probed (left). From the integral of the difference of the absorption spectra for both polarities of either circularly polarized light or magnetic field, orbit and spin momentums can be derived (right).

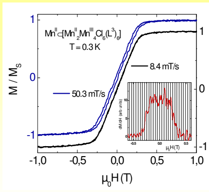
$$\mu_S \propto (3p-2q)\cdot\mu_b \qquad \mu_L \propto q\cdot\mu_b$$





Molecular nanomagnets

Molecular magnets are considered to be promising candidates for the observation of macroscopic quantum coherence effects. They could be utilized as quantum bits (qbits) being the basic elements of quantum computers, or for high density magnetic information storage. The (antiferro-)magnetic coupling of the paramagnetic ions in the molecular nanomagnets, presumably through the oxygen atoms of the ligands, gives rise to this effect. However, the coherence time, i.e. the time for which quantum information is stored in a molecule, is limited by phonon coupling and other not yet fully understood effects[4] and so far relevant only at temperatures in the 100 mK regime.



Mn_7-supramolecules show magnetic spin tunneling in torque magnetometry

XMCD results (BESSY, PM-3 beamline)

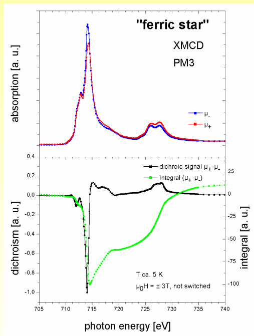
The samples were prepared by dropping chloroform solutions onto Si wafers yielding thin films.

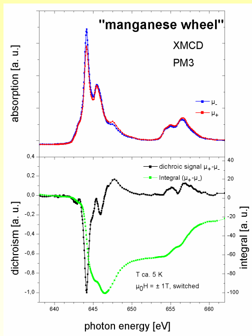
The absorption signal stems from measurement of the total electron yield. The μ_+ and μ_- spectra were gained by reversing the magnetic field either after one complete spectrum (fast) or every data point (slow, but same exposition time for each data point pair). Reversing the helicity instead was not exact enough due to miscalibration of the zero point.

The substances of interest have different ground state spins due to different coupling patterns of the ions:

- „ferric wheel“: each ion coupled (antiferromagnetically) to its next neighbour; S = 3*(5/2)-3*(5/2) = 0
- „ferric star“: center ion coupled to each of the three ions at the edges; S = 3*(5/2)-(5/2) = 10/2
- „manganese wheel“: not definitely known yet

Due to the lower flux of the dipole beamline (10^{-4}…10^{-3}) the degradation as an effect of radiation plays a much smaller role than in normal NEXAFS or STXM measurements at undulator beamlines.





If some simplifying assumptions hold (which is usually the case for transition-state metals and 2p-3d transitions), the aforementioned sum rules allow to calculate the ratio of orbit vs. spin momentum. The error for the orbit momentum is quite high, though.

$$\mu_L : \mu_S = 1 : -20{,}6 \qquad \mu_L : \mu_S = 1 : +20{,}3$$

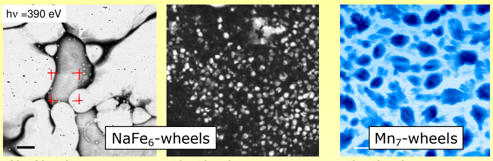
The XMCD studies (performed at around 5 K for the metal L-edges) show a distinct dichroic signal, which is, however, purely due to the interaction of the paramagnetic ions with the magnetic field and not due to magnetic correlations within the molecules or even inter-molecular interactions. The same is true for the momentum ratio.

To be able to investigate correlation effects would require temperatures as low as 300 mK (depending on the molecule) which we could not achieve in the presently available setups. Furthermore, the experimental data (NEXAFS and XMCD) for Mn_7 can only be analyzed on the basis of convenient theoretical calculation due to the mixed valence of manganese, which has yet to be done.

NEXAFS and STXM results (ALS, STXM BL 5.3.2, BL 11.0.2)

The samples were prepared by dropping chloroform solutions onto Si wafers (for NEXAFS) and Si_3N_4 membranes (for STXM). The morphology of the thin films depends strongly on the conditions during preparation. Quick evaporation of the solvent yields polycrystalline films with grain sizes below 200 nm (center, right). Slow evaporation of the solvent (e.g. in chloroform atmosphere) results in rather homogenous films (left image).

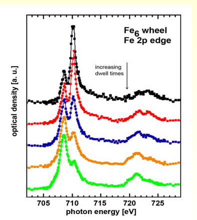
The intensity change inside the red marked square demonstrates the effect of radiation damage in a previously scanned area (see time-dependent studies).

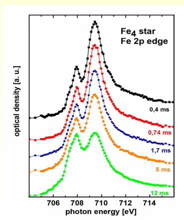


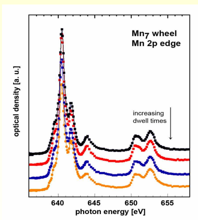
30 x 30 µm² 10 x 10 µm² 40 x 40 µm²

Time-dependent studies (ALS STXMs, BESSY UE52-PGM)

The NEXAFS absorption signal was recorded by measurement of the total electron yield (sample current) or partial auger yield (partial yield detector). In the STXM, the spectra were recorded as line scans with one data point per sample position.







For the „ferric wheel“ and „ferric star“, a strong influence of the radiation dose on the intensity distribution between the two main Fe resonances can be observed. The growing intensity of the resonance at lower energy which is allocated mainly to Fe^{II}[5] suggests a photon-induced reduction. This strong radiation damage is attributed to inefficient core hole screening in these weakly bound supramolecular aggregates. STXM allows much shorter irradiation times (<100 µs) which may circumvent this problem. The „manganese wheel“ spectra, however, do not show a significant change upon exposure in contrast to previous data for the „Mn_{12}“ compund[6].

Conclusion

Sample preparation has great effect on the morphology of the resulting thin films and has yet to be optimized and controlled in a better way.

Namely the iron compounds are prone to radiation damage. For further investigations, low flux or very fast measurement techniques have to be applied.

Prospective XMCD measurements have shown very promising results. However, in order to detect quantum correlation effects, measurement at a lower temperature has to be implemented.

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