Introduction

We have investigated the electronic structure of supramolecular clusters with NEXAFS spectroscopy. For laboratory 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\textsubscript{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 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.

Our model substances (Synthesis: AK Saalfrank, OC Univ. Erlangen, Germany)

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 (qubits) 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 not yet fully understood\cite{1} and so far only relevant at temperatures in the 100 mK regime.

NEXAFS and STXM results (ALS, STXM BL 5.2.2, BL 11.0.2)

The samples were prepared by dropping chloroform solutions onto Si wafers (for NEXAFS) and SiSi 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 (carbon black). Slow evaporation of the solvent (e.g. in chloroform atmospheres) results in rather homogenous films (left image).

The absence of any electronic transitions at the K and L edges of the Fe ions in the Mn\textsubscript{6}Fe\textsubscript{4} and Mn\textsubscript{6}Fe\textsubscript{4} wheels confirms the absence of L\textsubscript{2,3} transitions, which are due to the Fe ions.

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\textsuperscript{2+} suggests a photon-induced reduction. This strong radiation damage is attributed to insufficient 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 in contrast to previous data for the Mn\textsubscript{6} ion, which was investigated\cite{2}.

XMCD results (BESSY, FM-3 beamline)

The XMCD studies (performed at around 5 K for the metal L\textsubscript{2,3} 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.

The XMCD results show that the Mn\textsubscript{6}Fe\textsubscript{4} and Mn\textsubscript{6}Fe\textsubscript{4} wheels can be distinguished from each other. The XMCD signal for the Mn\textsubscript{6}Fe\textsubscript{4} wheel is stronger than for the Mn\textsubscript{6}Fe\textsubscript{4} wheel. This observation is in agreement with the NEXAFS results.

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 may 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.

References

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