

How Can X-ray Studies Contribute to the Field of Molecular Magnets

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Overview

- **From the atom to the cluster: The influence of the bonding**
The characterization of the electronic state
- **The local symmetry and structure: The influence of ligands, solvents, and more**
The structural characterization (preparation)
- **Each molecule is different: The example of Mn₁₂Ac**
(X-ray)-Experiments, which can probe the magnetism of Mn₁₂Ac
- **Conclusion: Different techniques have to be combined**
How can the APS give considerations to this



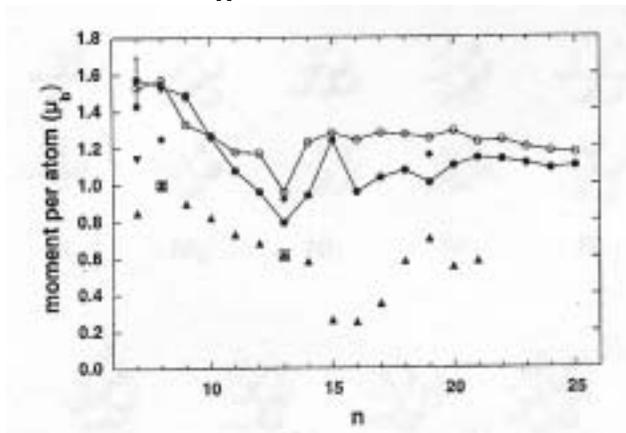
From the Atom to the Cluster: Various X-ray based Techniques

- **X-ray Absorption Fine Structure (XAFS) Spectroscopy:**
 - valence state (soft & hard X-rays)
 - electronic configuration / multiplet / low significance
 - electron density/empty states (soft & hard X-rays)
- **Diffraction Anomalous Fine Structure (DAFS) Spectroscopy:**
 - Similar to hard X-ray XAFS but with q-resolution
- **X-ray Magnetic Circular Dichroism (XMCD) Spectroscopy:**
 - Spin/orbit contribution of the magnetic moment (soft x-rays)
 - Element selectivity of magnetization
 - Multiplet-information
- **Resonant Inelastic X-ray Scattering (RIXS):**
 - Similar to XAFS but with a high significance
- **X-ray Raman Scattering:**
 - Similar to soft x-ray XAFS but with X-ray energies ~10KeV

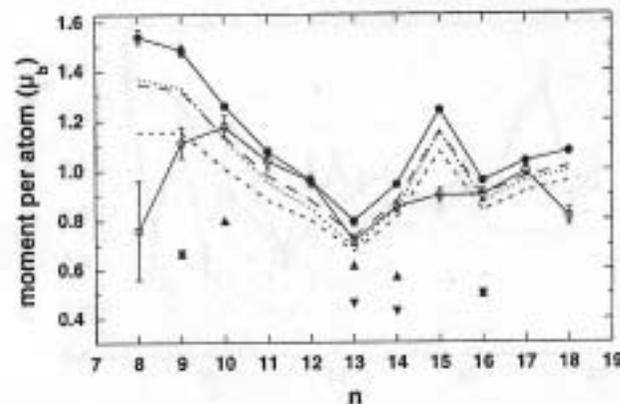


From the Atom to the Cluster: Ni-Clusters & Ligands

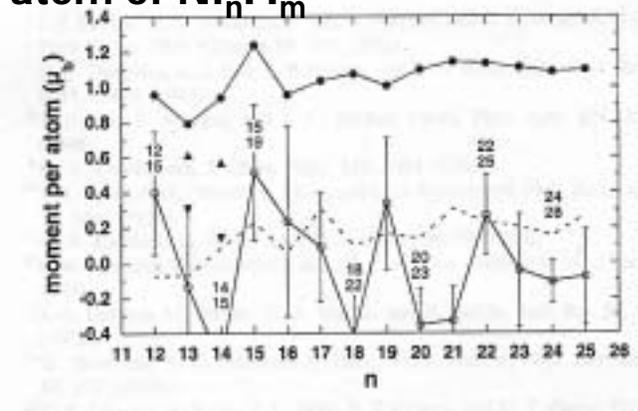
Magnetic moments per atom of Ni_n



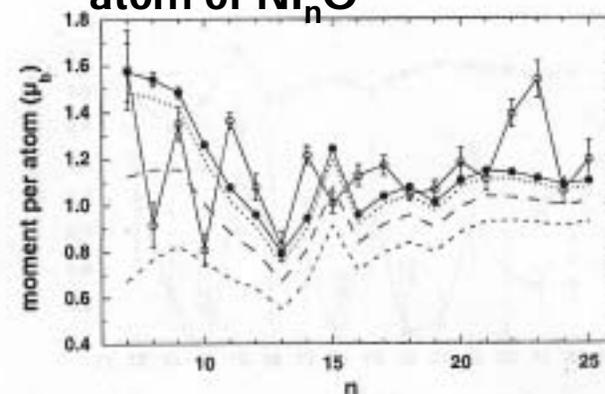
Magnetic moments per atom of Ni_nCO



Magnetic moments per atom of Ni_nH_m

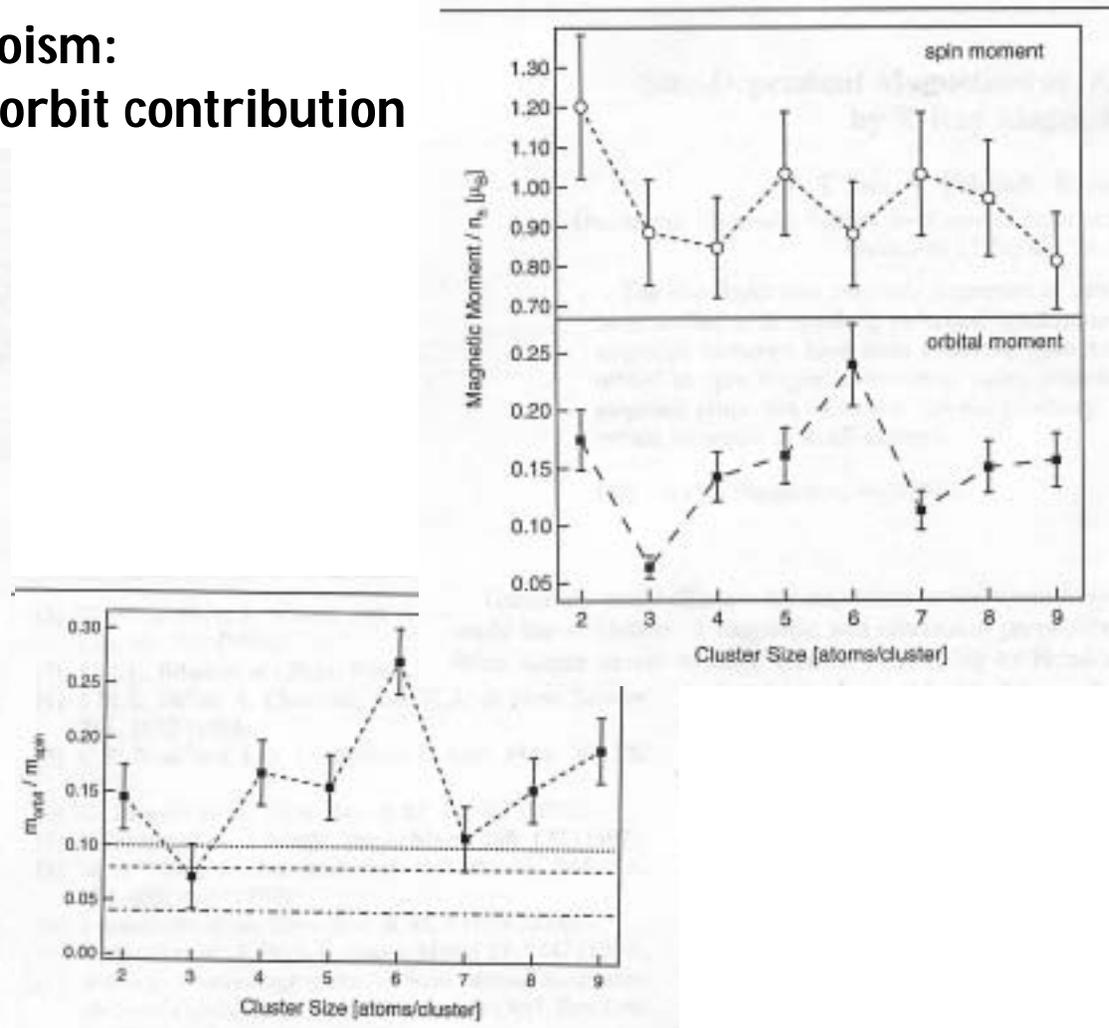
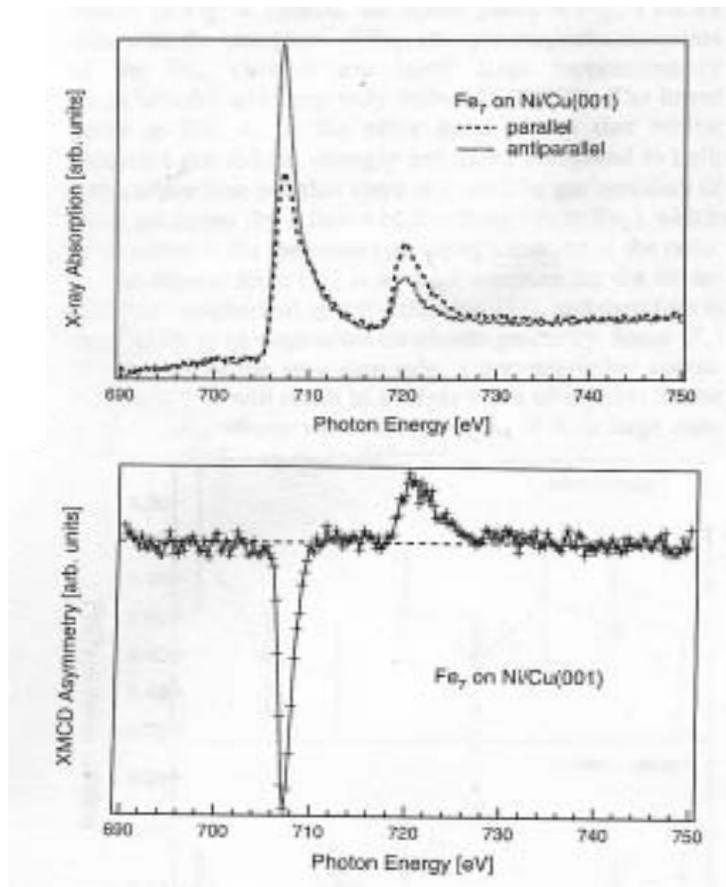


Magnetic moments per atom of Ni_nO



From the Atom to the Cluster: Fe-Clusters and It's Magnetic Moment

X-ray Magnetic Circular Dichroism:
A way of determining the spin/orbit contribution

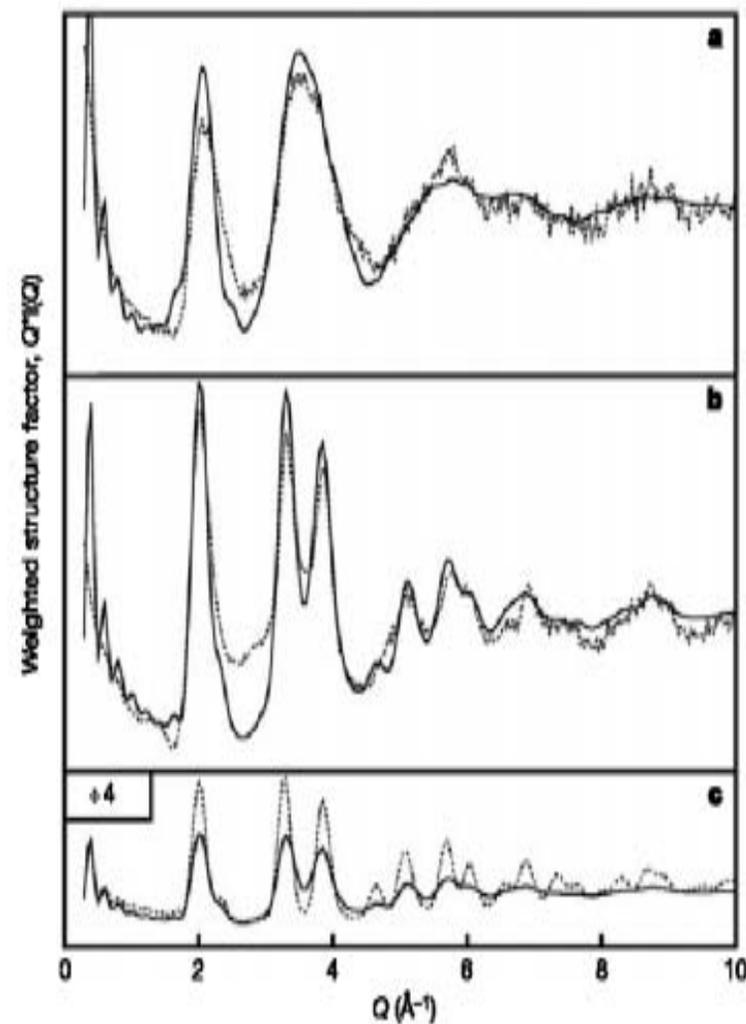
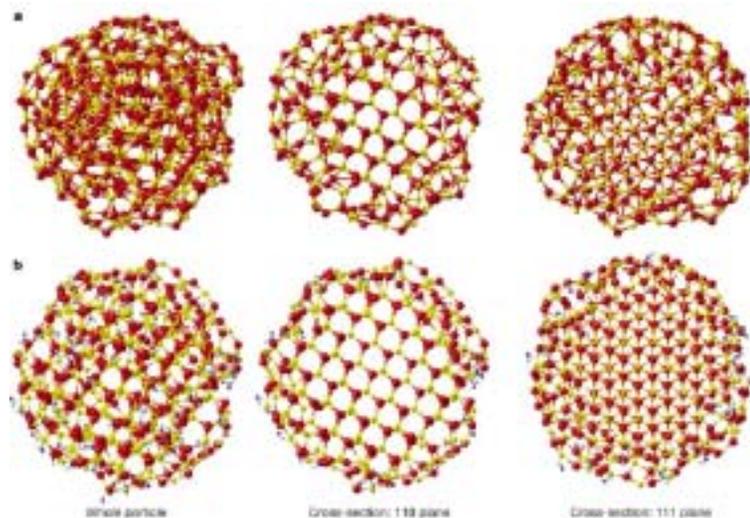
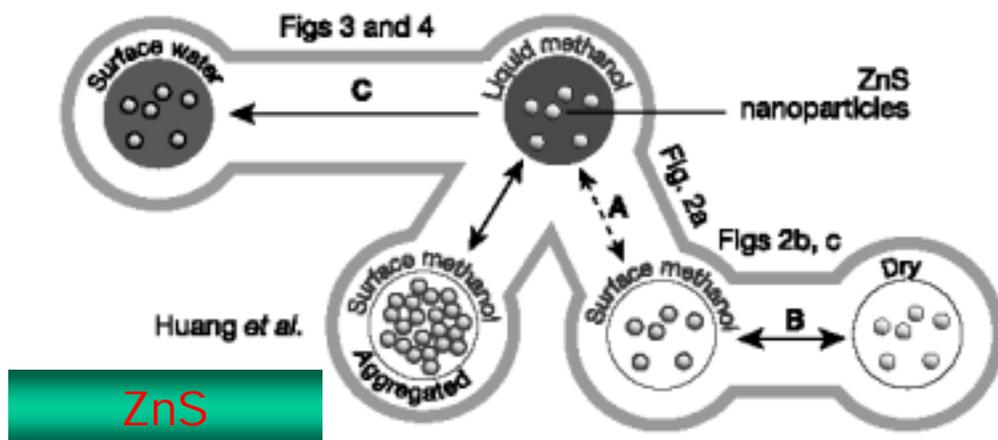


The local symmetry and structure: Various X-ray based Techniques

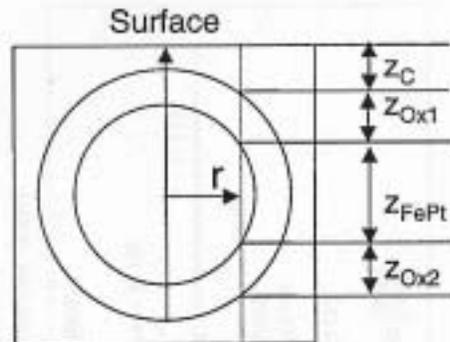
- **Local structure:**
 - X-ray Absorption Fine Structure (XAFS)
 - Extended X-ray Absorption Fine Structure (EXAFS)
 - Pair Distribution Function (PDF)
 - X-ray Standing Wave (XSW)
- **Global structure/symmetry:**
 - X-ray diffraction (XRD)
 - Powder Diffraction (PDF)
 - Surface Diffraction
- **Shape**
 - X-ray microscopy
 - Small Angle X-ray Scattering (SAXS)



The influence of ligands, solvents, and more PDF shows structure of ZnS nano particles

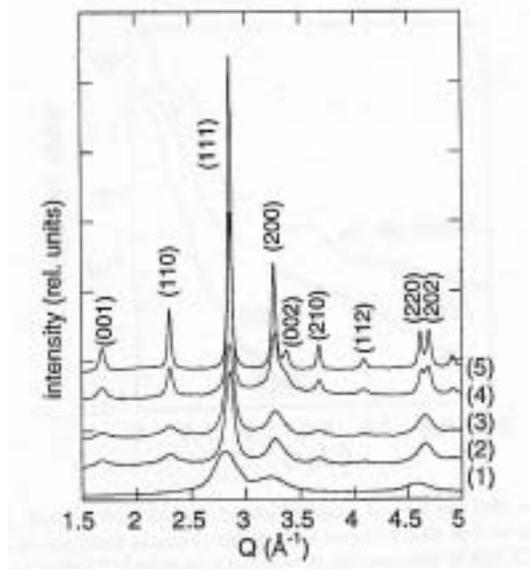


The influence of ligands, solvents, and more XAFS & XRD characterize nano particles

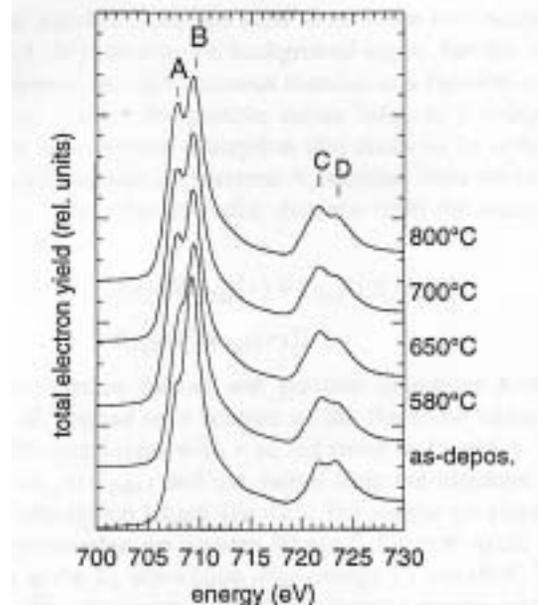


Resulting Model

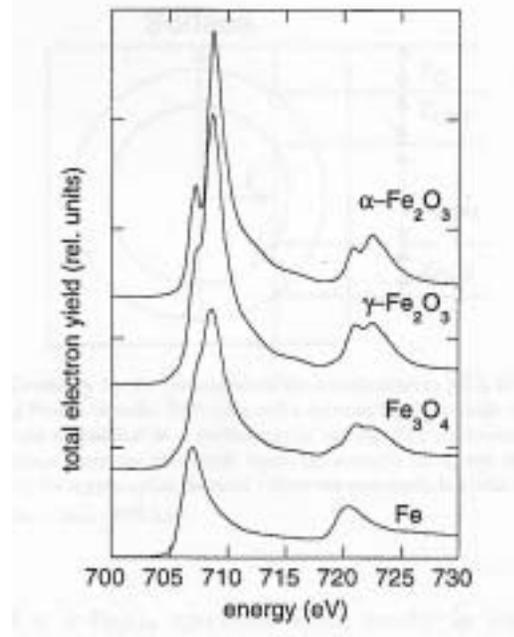
XRD Data



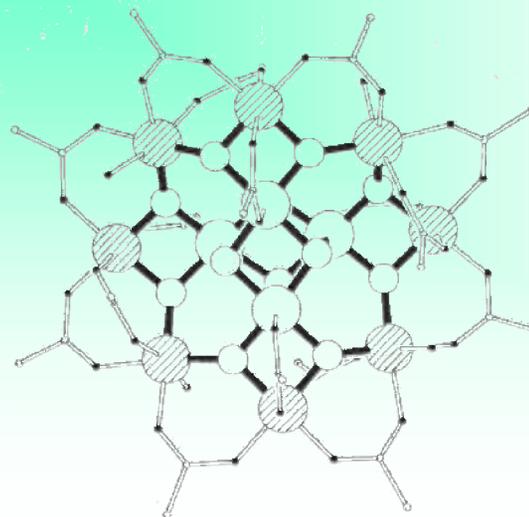
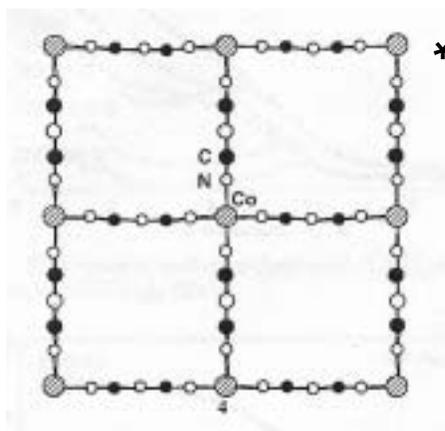
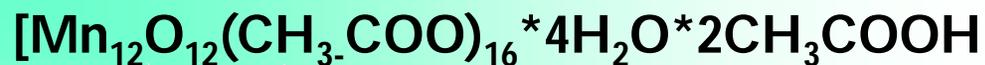
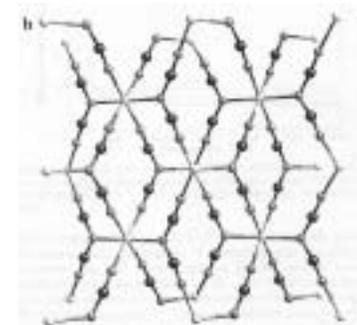
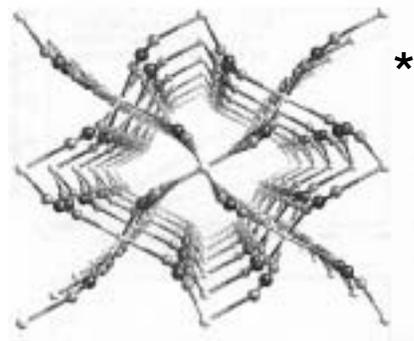
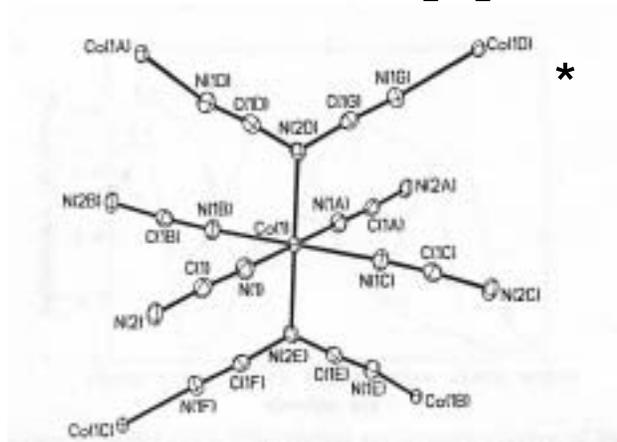
XAFS Data



Reference Spectra



Each molecule is different: The example of Mn12Ac

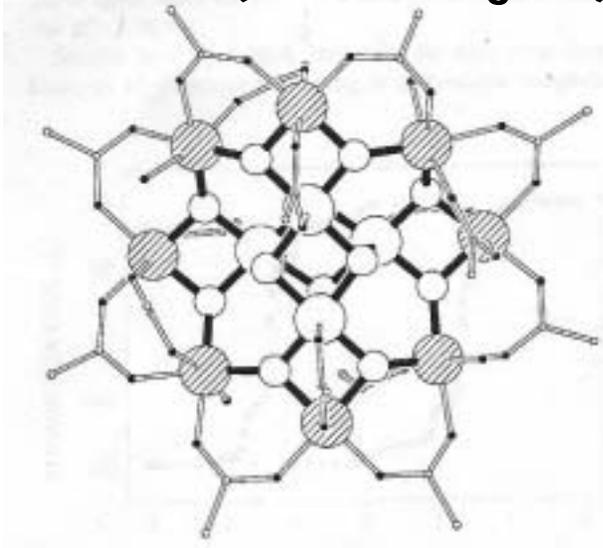


Mn12Ac

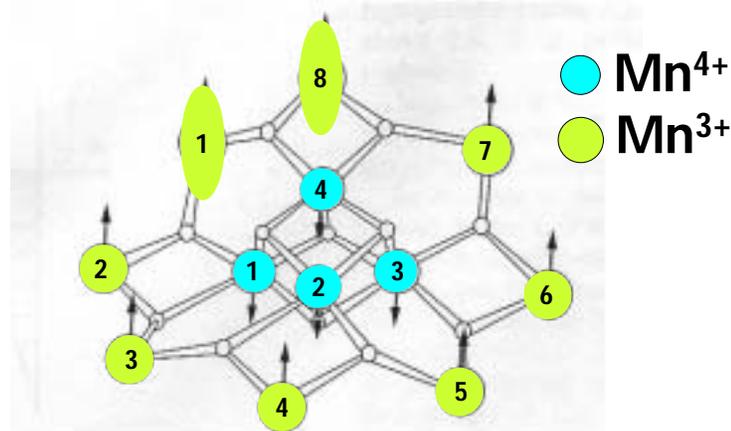


Each Molecule is Different: Structure and Magnetic Moment

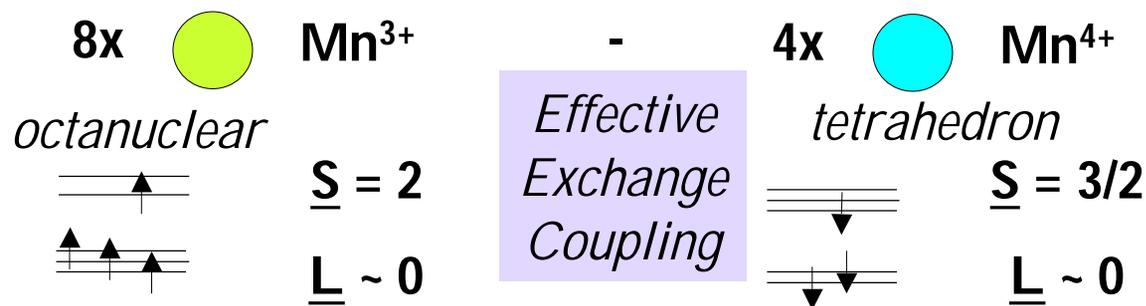
Mn12Ac (inclusive ligand)



Mn12Ac
(only Mnⁿ⁺ and O²⁻ positions)



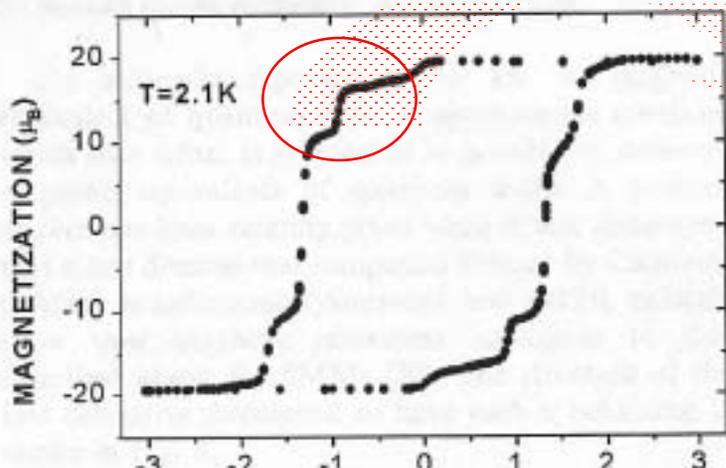
The Magnetic Moment per Molecule:



Total Magnetic Moment / Molecule:

$$\begin{aligned}
 M &= 2 * S * \mu_B \\
 &= 2 * (8 * 2 - 4 * 3/2) \mu_B \\
 &= 2 * 10 * \mu_B
 \end{aligned}$$

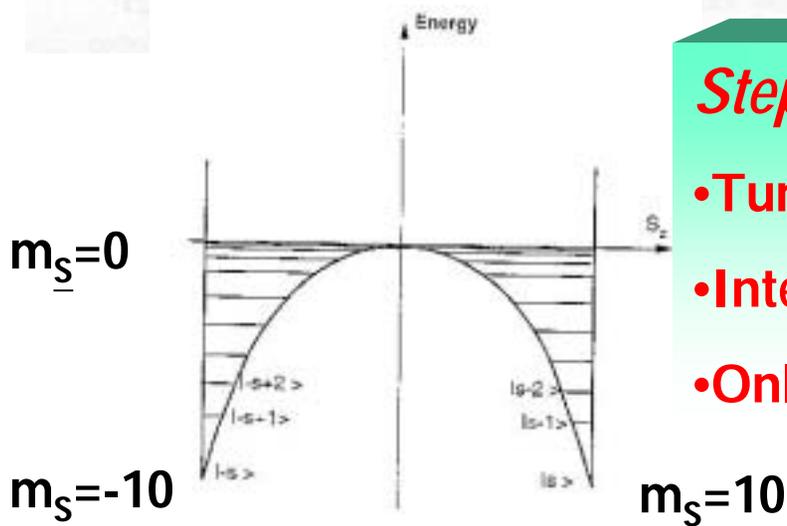
Each Molecule is Different: The Magnetic Properties



Full Magnetization : $\pm 20\mu_B$

Step-like Behavior: Tunnel Effect!

Thermal Behavior: $\Delta_0 \exp(\Delta/kT)$
 $\Delta_0 = 2 \times 10^{-6} \text{ s}$ $\Delta/kT = 62 \text{ K}$



Step-like Behavior can be explained by:

- Tunneling effect
- Interaction between molecules have to be $\sim \underline{S}^2$
- Only possible, if exchange coupling through ligand



The example of Mn12Ac

What X-ray Experiments can be done?

Problems:

- Influence of the ligand on the electronic state of Mn
- Influence of the ligand on the magnetic behavior of the molecule
- How large is the orbital contribution
- Correlation of the magnetization (M_S) with the multiplet structure of Mn
- Correlation of the magnetization (M_S) with lattice deformations
- Nature of the exchange interaction between the molecules

XMCD @ Mn
L- & K-Thresholds
with various ligands

XMCD @ Mn
L-Thresholds
with various
magnetic fields

RIXS @ C
K-Threshold
XMCD @ C
K-Threshold

EXAFS @ Mn
K-Thresholds
Anomalous XRD
Diffuse XRD

Conclusion: ***Different techniques have to be combined***

Sample preparation & characterization

- Various scattering techniques (global symmetry)
- EXAFS (local distortions)
- XAFS (valance state & electronic properties)

Characterization of the magnetic behavior

- XMCD @ L-Threshold of 3d elements
- XMCD @ K-Threshold of 3d elements
- XMCD @ K-Threshold of C (RIXS)
- EXAFS @ K-Threshold of 3d elements

Requirements:

- Combination of various techniques
- Strong theoretical support
- Extreme sample conditions
- Easy and fast access during sample preparation
- Network of experts (of various techniques)

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Some Literature

Molecular Magnets:

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