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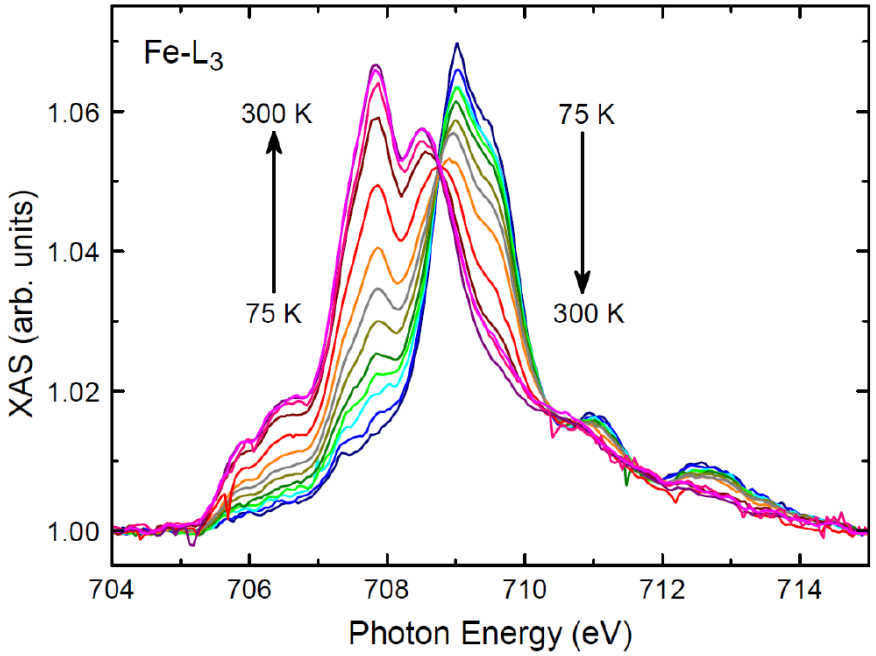

Spin Crossover In A Vacuum Deposited Submonolayer Of A Molecular Iron(II) Complex

Influenced by the same-titled paper of Matthias Bernien et al. | J. Phys. Chem. Lett. 2012, 3, 3431 - 3434

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History

- spin crossover effect was first observed in 1931 by Cambi et al.
  - 4 years before Schrödinger‘s equation
- spin states of these complexes are sensitive to their axial ligands
- later, by use of ligand field theory better understanding of the problem
- 1956, Orgel suggested a possible equilibrium of spin states as an explanation for the effect.
- today, the effect is well understood in bulk material and in solution
  - ultra thin layers are not yet investigated that extensively

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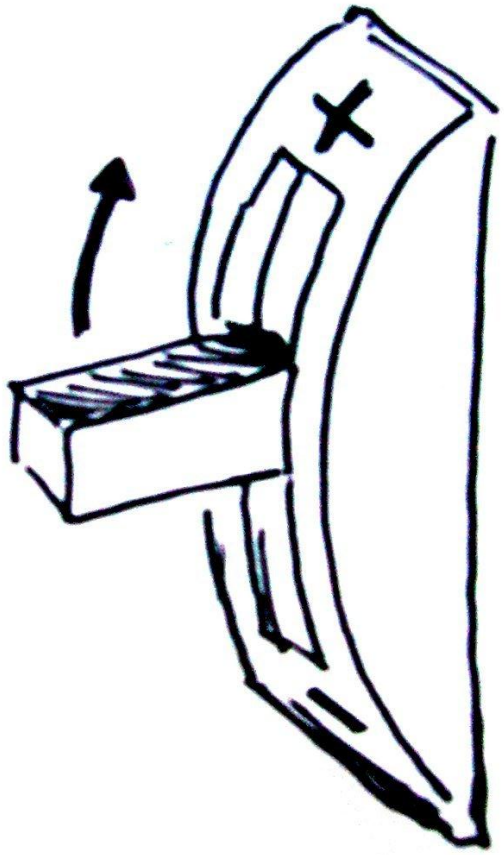
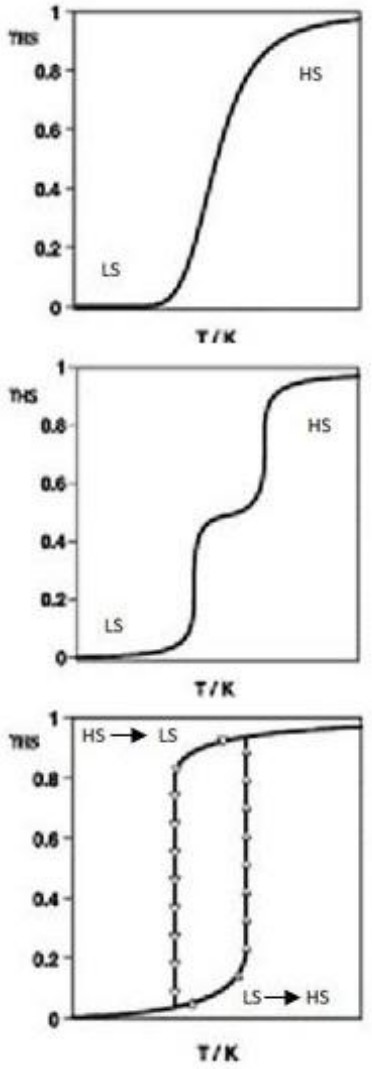


Future Applications

- many applications such as switches, data storage devices and optical displays due to intrinsic bistable spin states
  - ➢ abrupt spin transitions act as switching (ON or OFF)
  - ➢ size of data storage devices can be reduced, molecules carry information (1 or 0)
  - ➢ Gradual transition interpretet as color shift
- absence of fatigue



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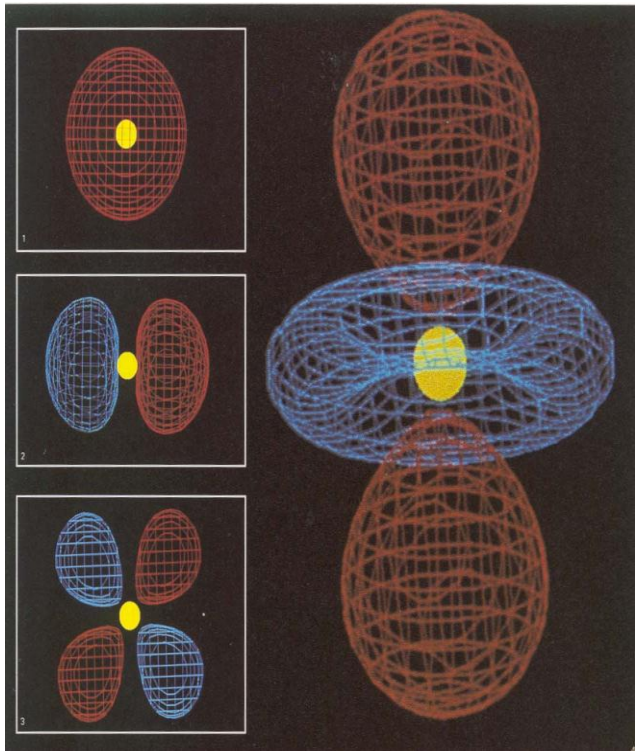
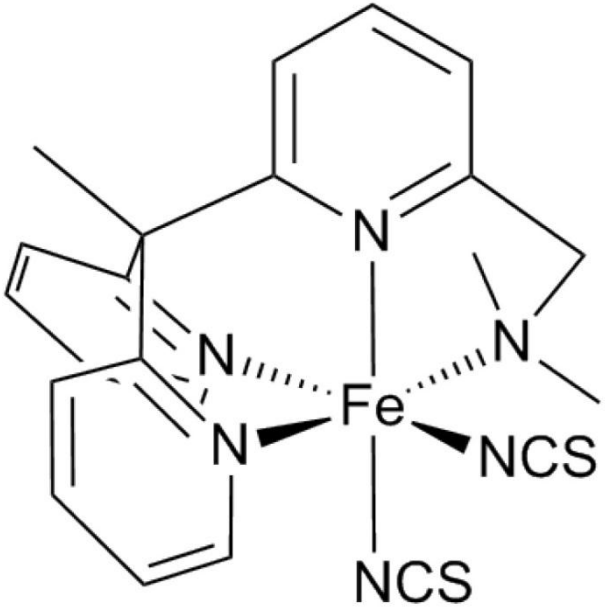


Fundamentals



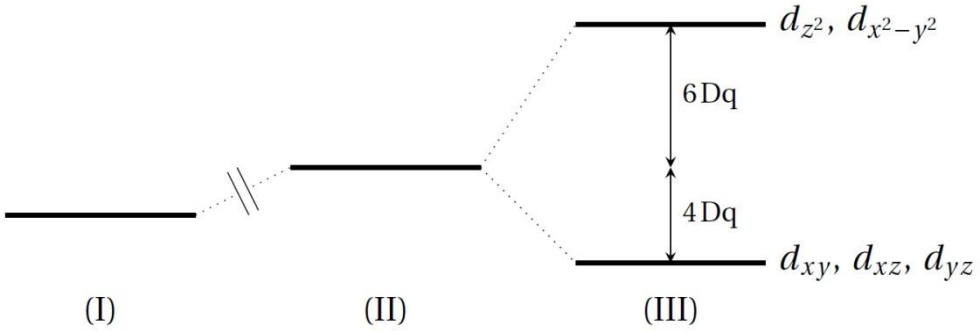
picture taken from Bernien et al. [I]

$Fe^{II}(NCS)_2$1-{6-[1,1-di(pyridin-2-yl)ethyl]-pyridin-2-yl}-N,N-dimethylmethanamine

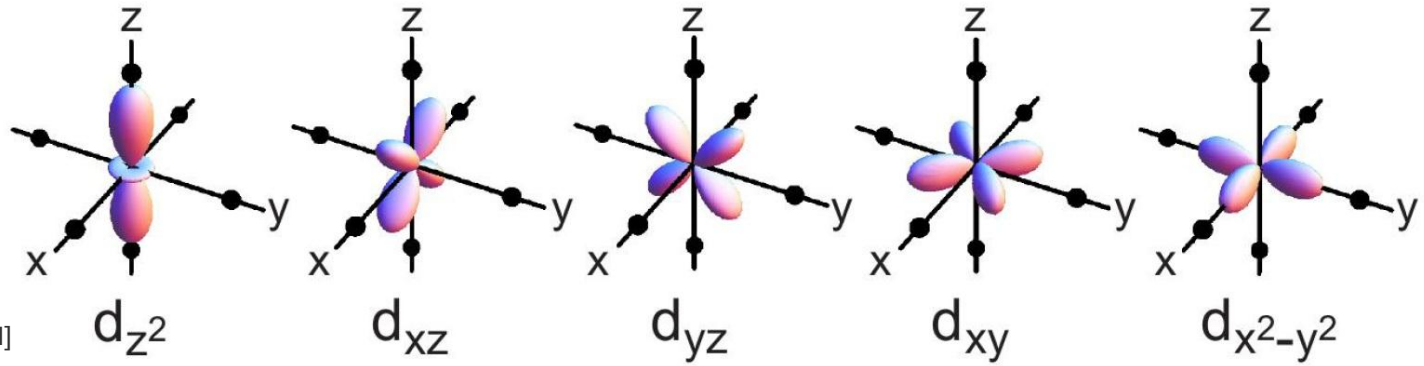
$Fe^{II}(NCS)_2L$

Ligand Field Theory

- electron configuration: [Ar] $3d^6$ ($4s^2$)
- energy levels are degenerate
- valence electrons interact with the surrounding ligands
- for strong splitting Hund‘s rule is not valid anymore



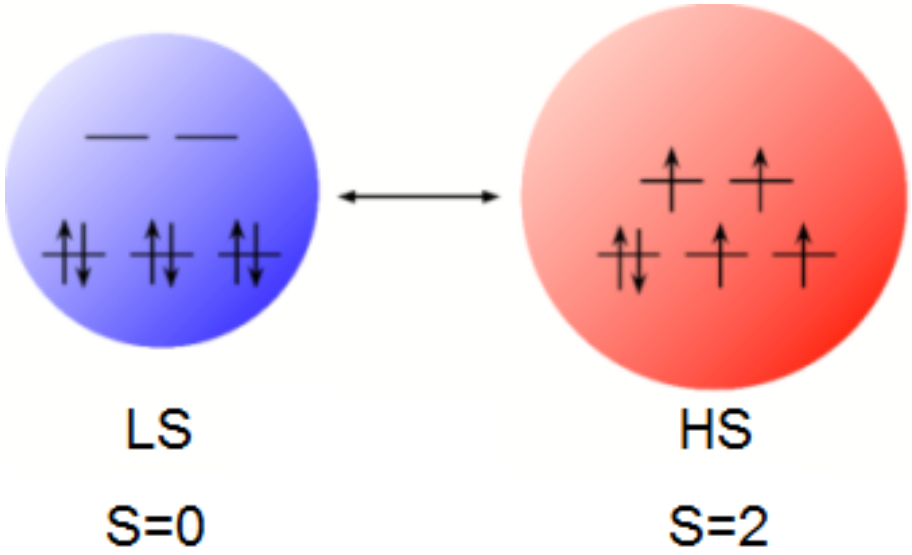
picture taken from Rolf [VII]



picture taken from Bernien [VIII]

Spin Crossover

- low spin (LS) state has major splitting
  - ➢ molecule is diamagnetic
- high spin (HS) state has minor splitting
  - ➢ molecule is paramagnetic
- splitting is also a function of the bond length
  - ➢ for low energy differences thermally induced spin crossover
- other perturbations possible



picture taken from
http://www.quimica.urv.es/w3qf/magnetisme/sco.html

Calculation Of Temperature Dependence

free enthalpy of the system $G = U - TS + pV$

free energy $F = \gamma \cdot F_{HS}(T) + (1-\gamma) \cdot F_{LS}(T) - T \cdot S_{Mix}$

$S_{Mix} = -k_B[\gamma \cdot \ln(\gamma) + (1-\gamma)\ln(1-\gamma)]$

equilibrium condition $\frac{\partial F}{\partial \gamma} = 0$

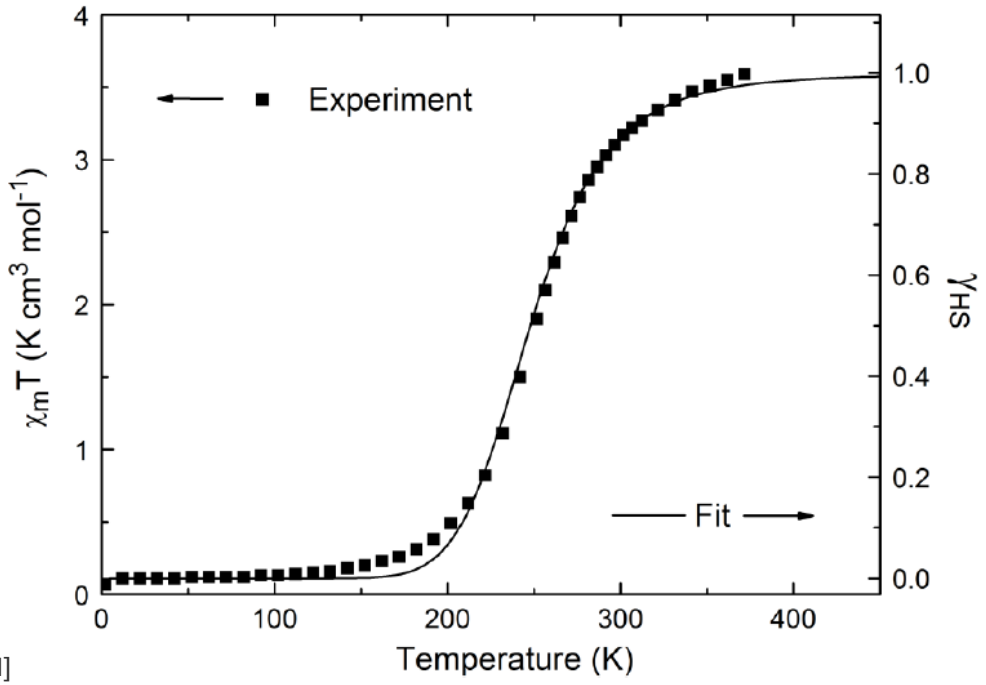
Calculation Of Temperature Dependence

$$\Delta F(T) = F_{HS}(T) - F_{LS}(T)$$

$$\Delta F(T) = k_B T \cdot \ln\left[\frac{(1-\gamma(T))}{\gamma(T)}\right]$$

$$\gamma(T) = \frac{1}{e^{-\frac{\Delta S}{k_B}} \cdot e^{\frac{\Delta U}{k_B T}} + 1}$$

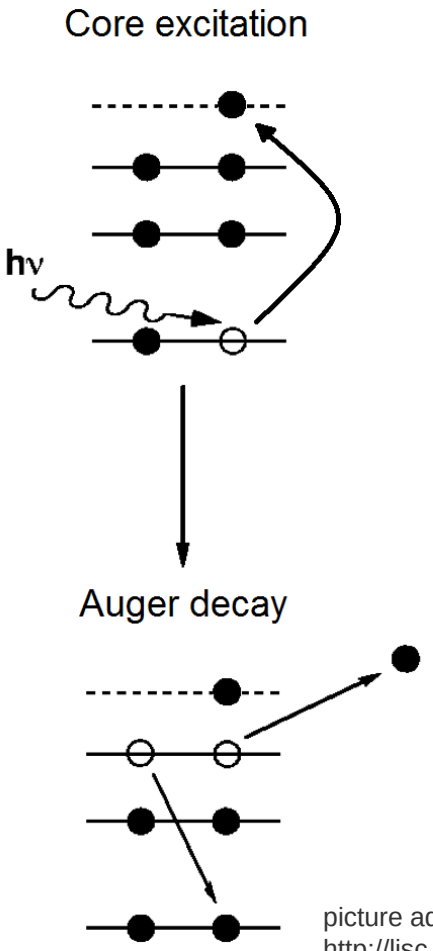
with $\Delta F = \Delta U - T\Delta S$



picture taken from Bernien et al. [I]

Near Edge X-Ray Absorption

- NEXAFS (*near-edge x-ray absorption fine structure)*
- investigates resonances at absorption edges
- displays the density of states at the edge
- all electrons are detected
  - ➢ TEY *(total electron yield).*



picture adapted from http://lisc.fbk.eu/solid-state-materials-science

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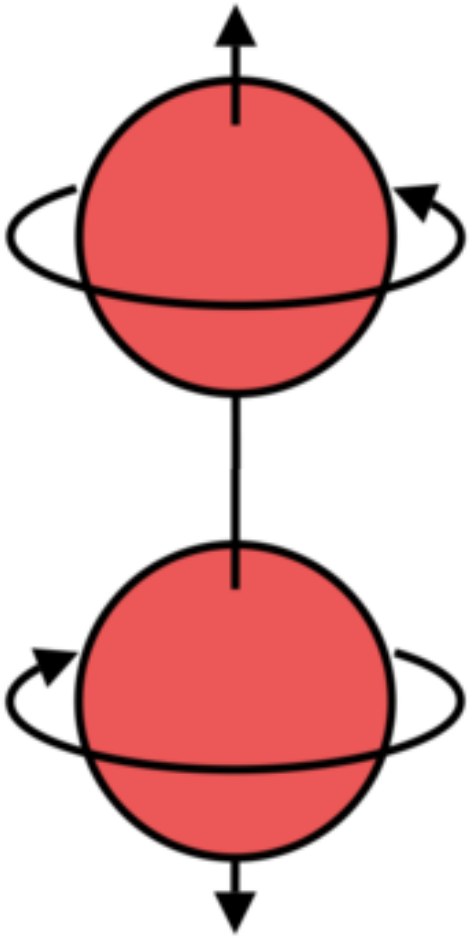
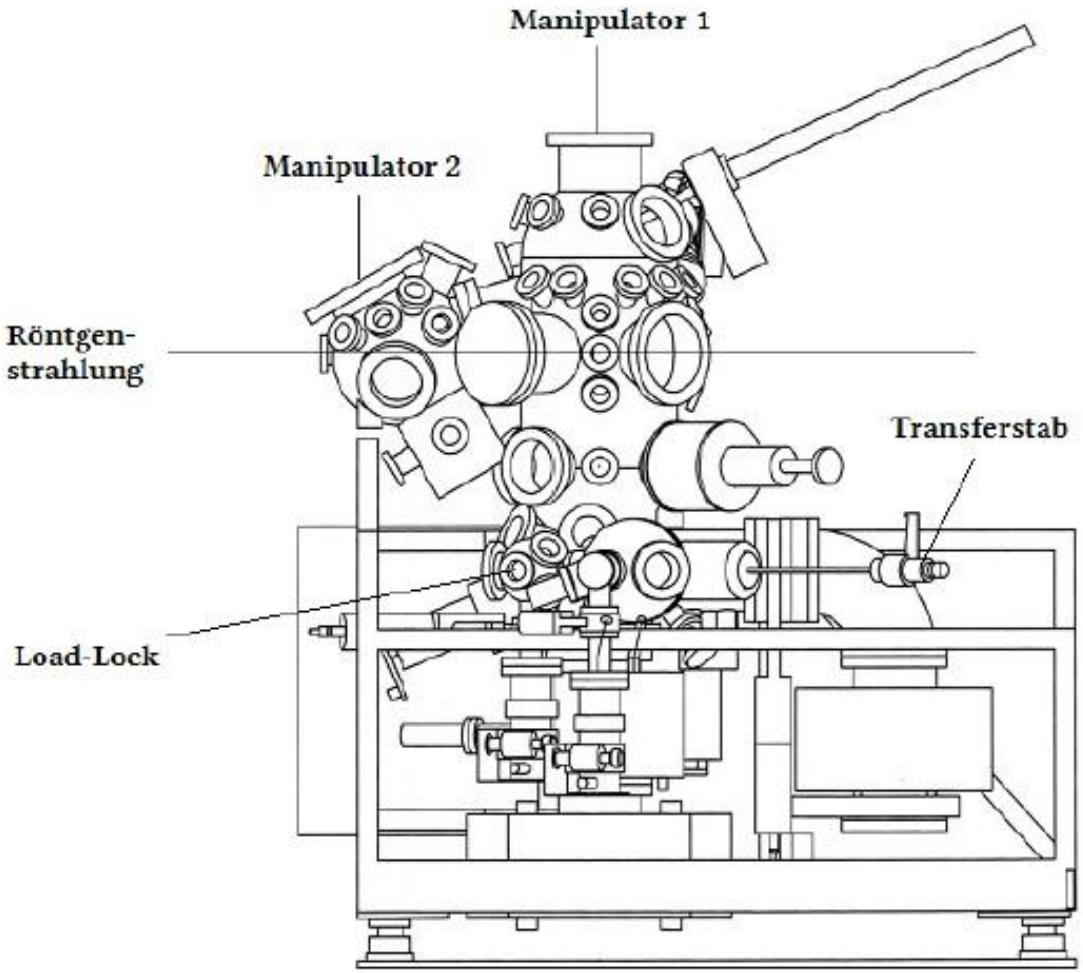
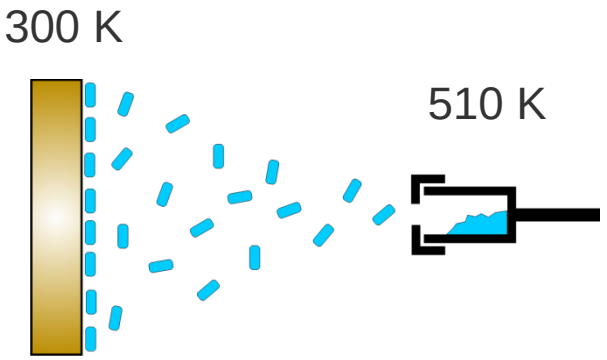


Setup Of The Experiment



picture taken from Rolf [VII]

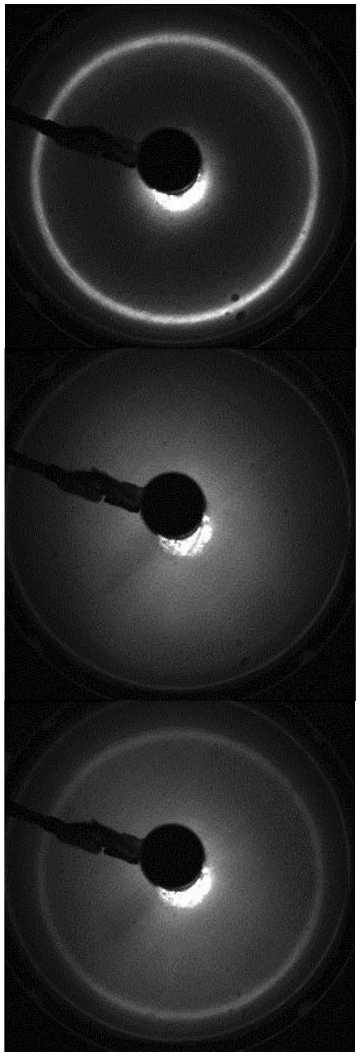


picture taken from
http://www.tuat.ac.jp/~usuilab/English/depo.html

Is It Really A Molecular Layer?

- highly oriented pyrolytic graphite (HOPG) as substrate
- very weak interaction with the molecules
- substrate diffraction pattern disappears
  - ➢ formation of a monolayer, no crystallization
- reappearance of the substrate diffraction pattern may be result of electron beam damage and subsequent partial desorption

clean surface

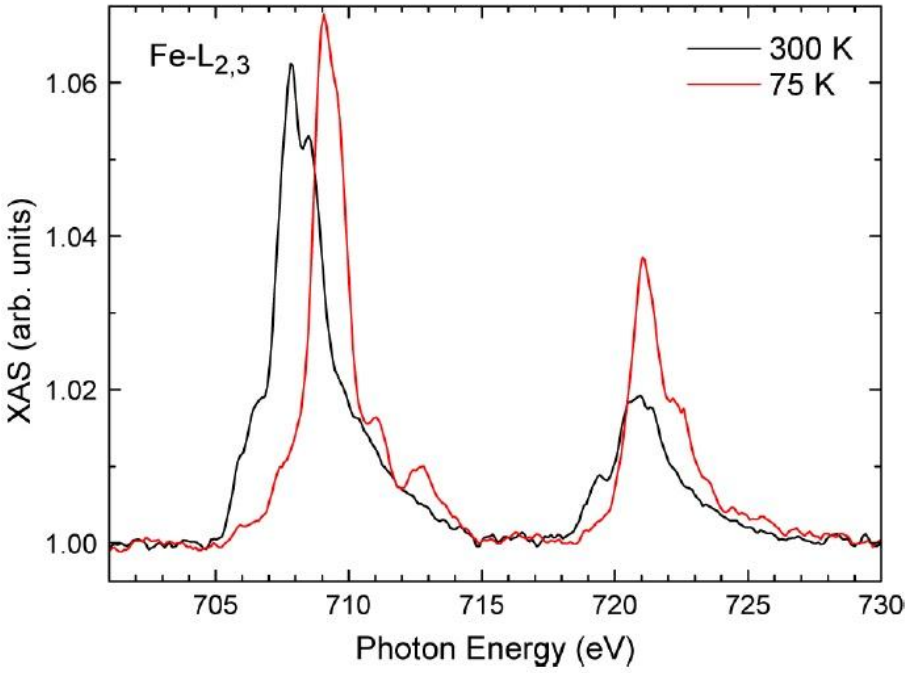


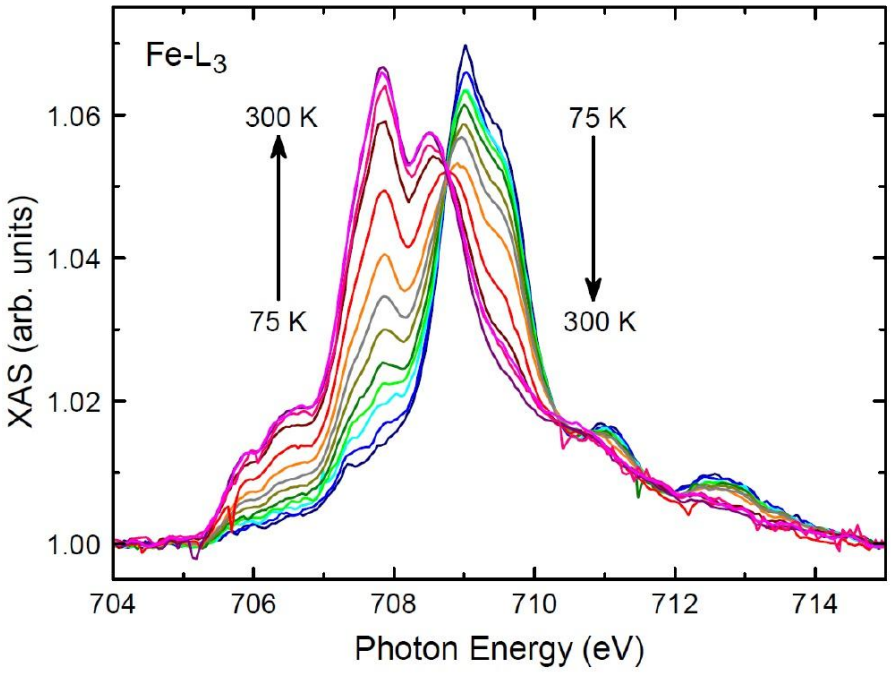
1.2 ML of $Fe^{II}(NCS)_2$

after 10min of exposure

picture taken from Bernien et al. [I]

Absorption Spectra



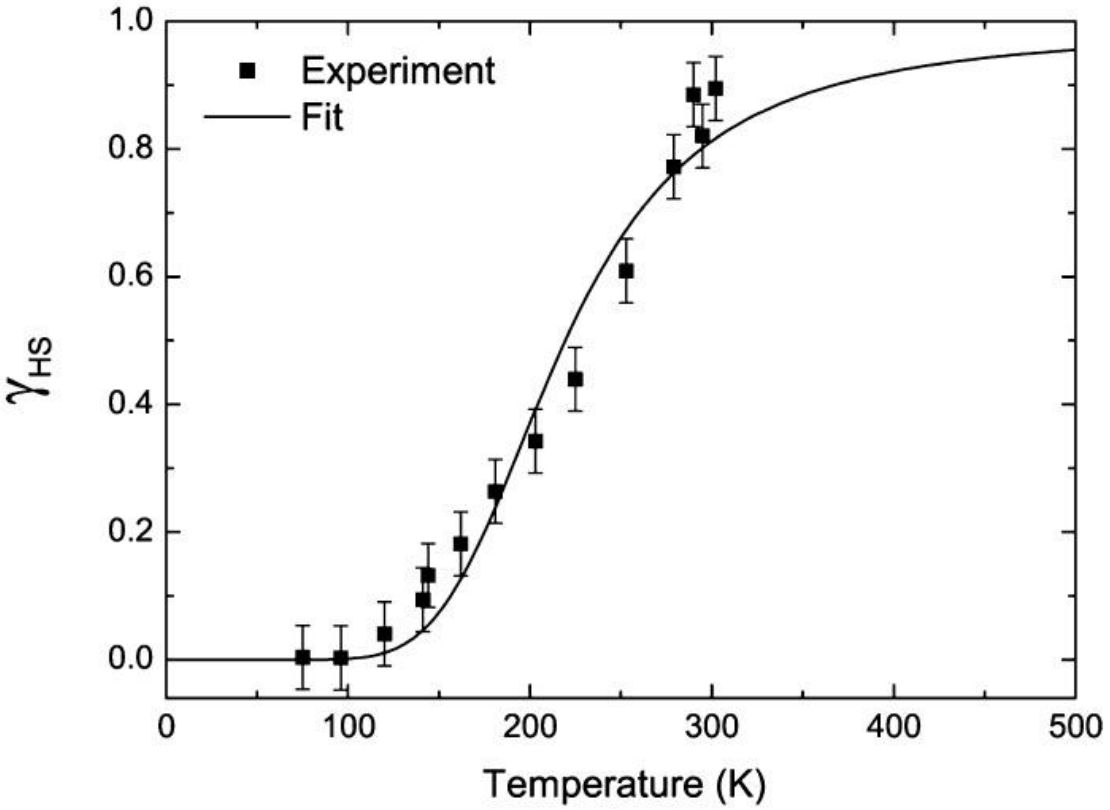


pictures taken from Bernien et al. [I]

- 0.8 ML $Fe^{II}(NCS)_2L$ on HOPG
- strong temperature-dependent change of lineshape
- proof of spin crossover effect taking place
- nearly complete interconversion

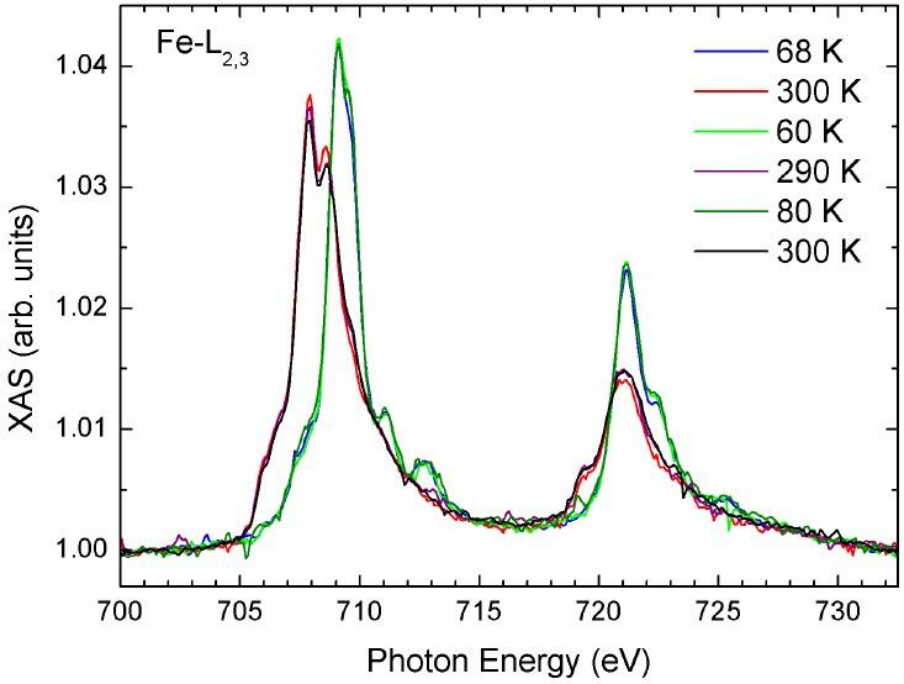
Temperature Dependence

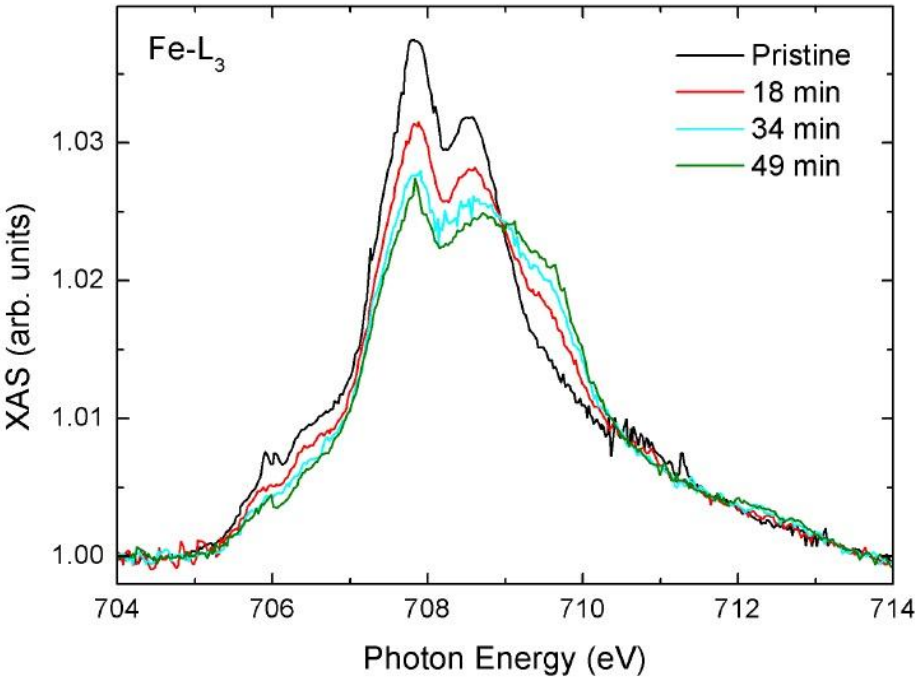
- transition temperature slightly lower than in the bulk measurement
- more gradual transition
  - ➢ less cooperativity



picture taken from Bernien et al. [I]

Reversibility





pictures taken from Bernien et al. [I]

- fully reversible for temperature variance
- for x-ray perturbation the sample undergoes an irreversible decomposition

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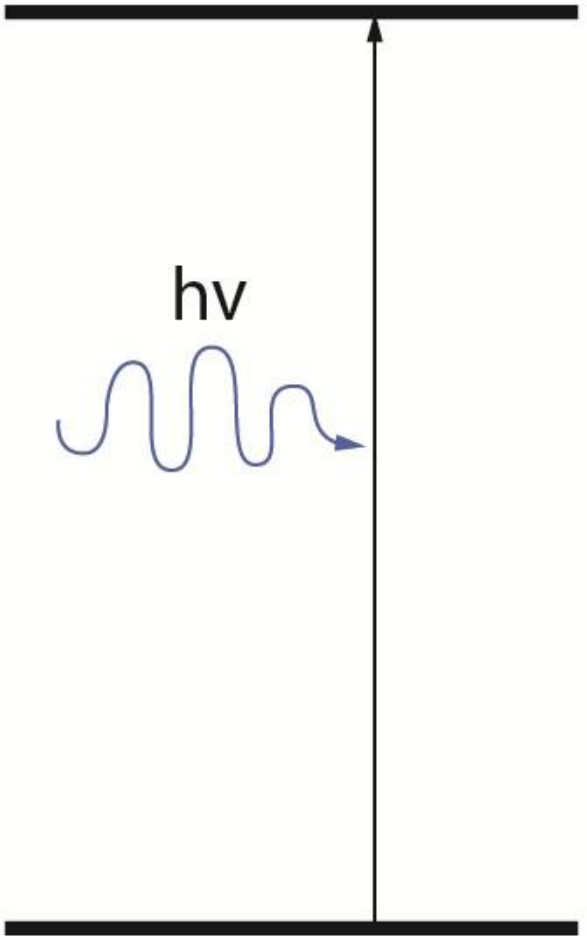
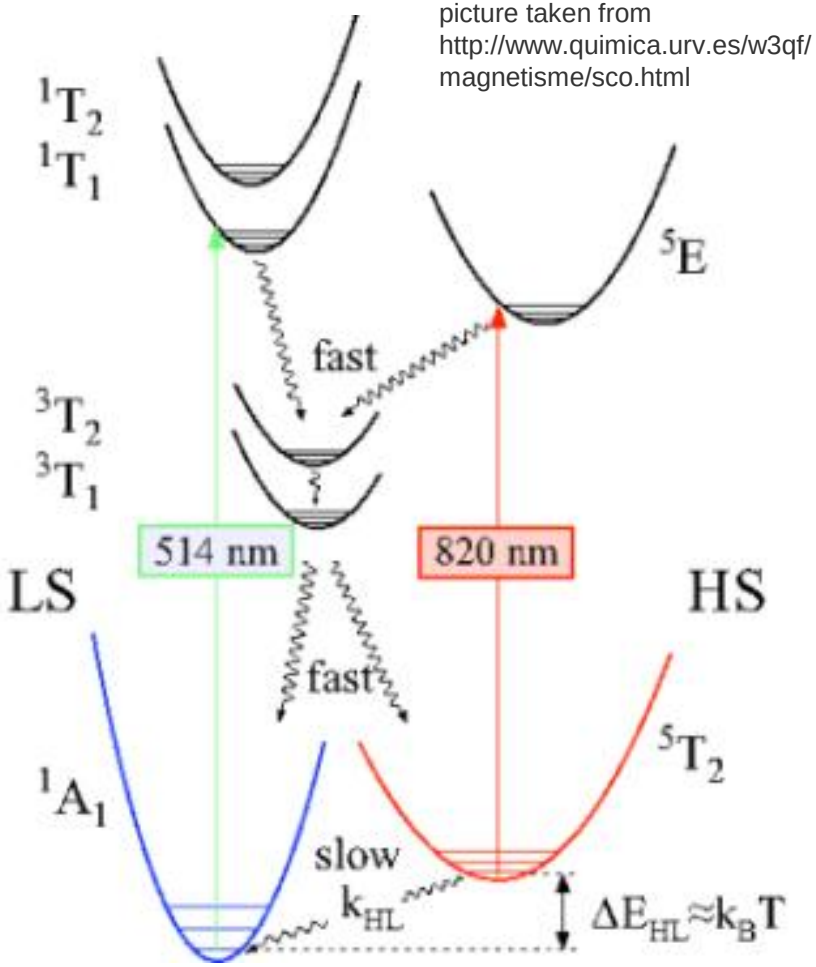


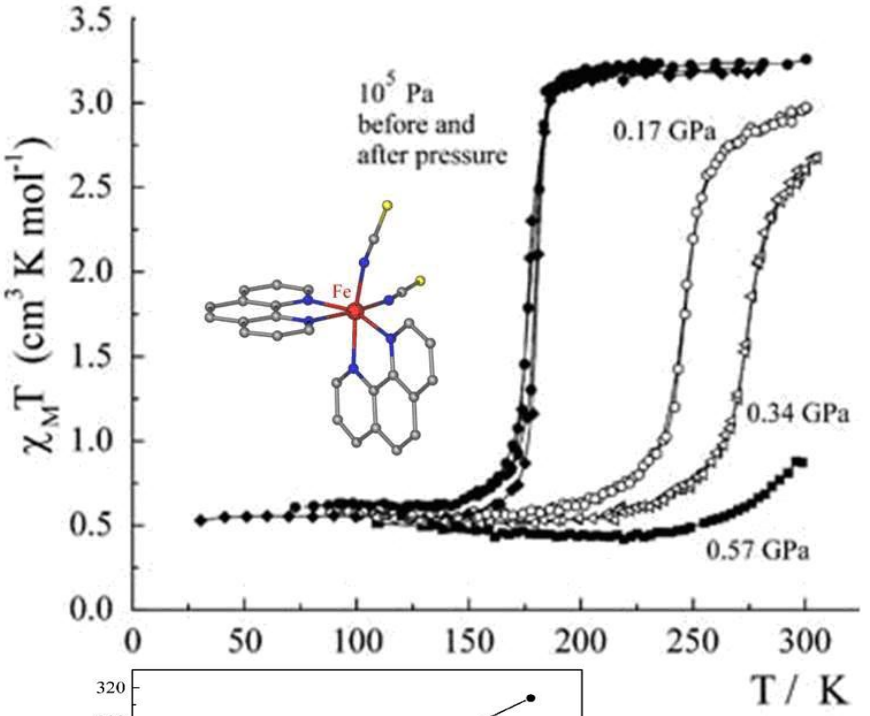
Light Perturbation

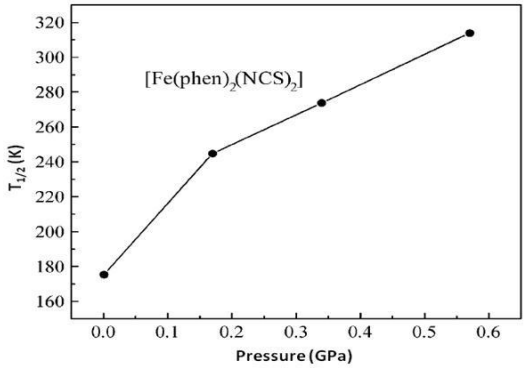
- HS and LS states can be triggered by irradiating the sample
- at low temperatures it is possible to trap compounds in the HS state
- reconversion to the LS state by irradiation with a lower energy light



Pressure Perturbation

- increase in pressure will decrease the volume of the unit cell
- difference in bond lengths in both HS and LS states changes the thermodynamic equilibrium of the system
- increase of the $T_{1/2}$ of the system
- fully reversible





pictures taken from Ksenofontov et al. [VI]

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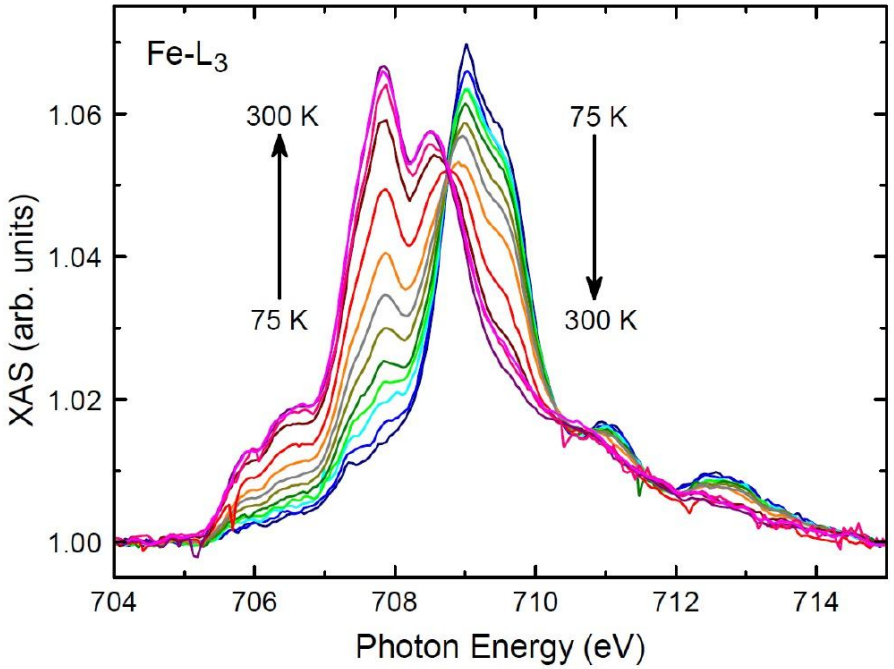
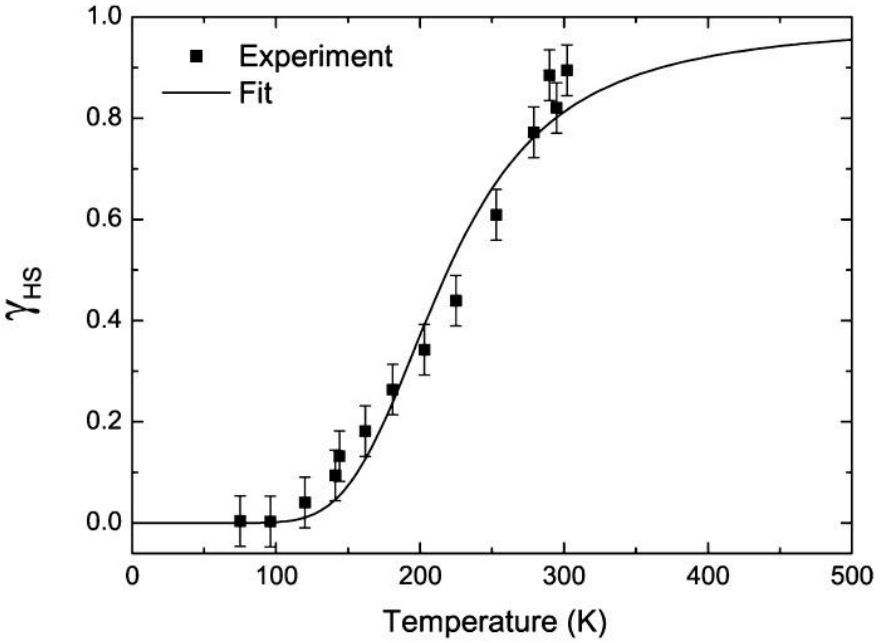
Summary





- very basic research
- need for more sophisticated materials

Still much work to do!

Content

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Any Questions?

Thanks for listening carefully