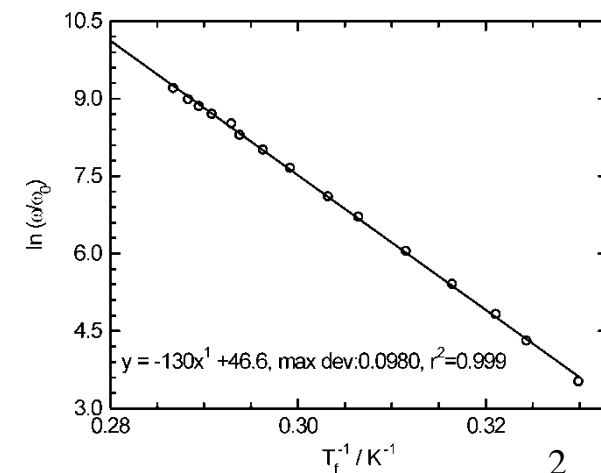
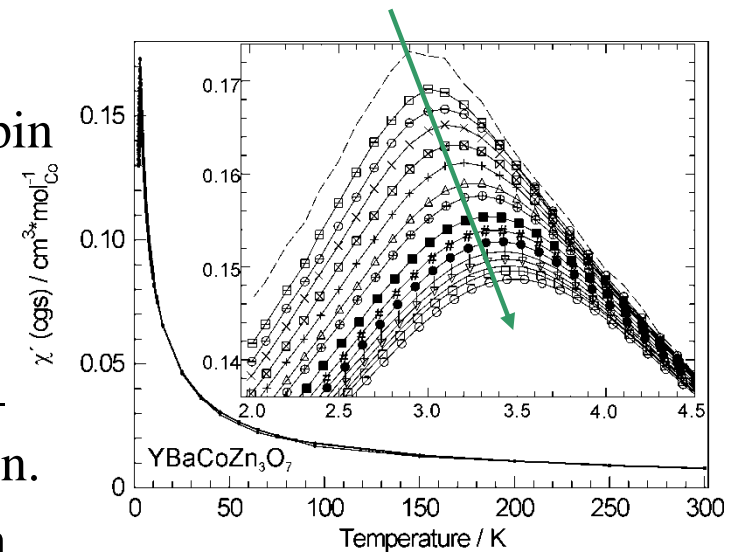
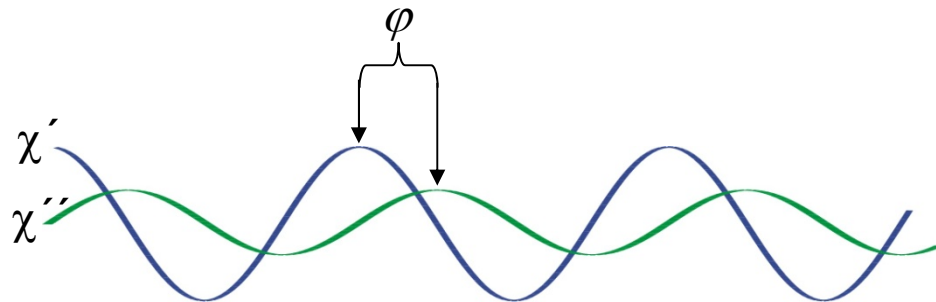
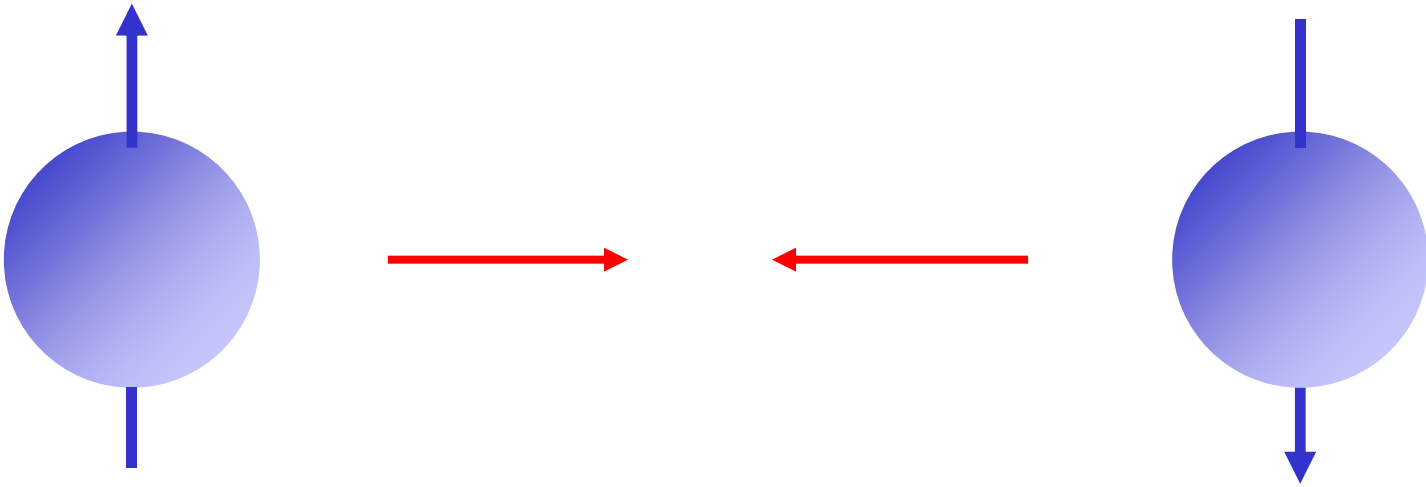




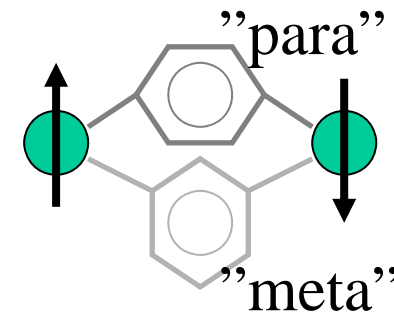
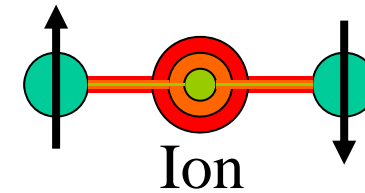
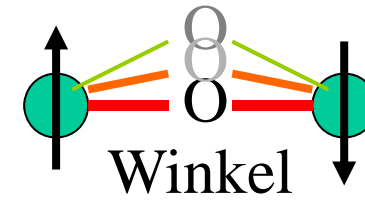
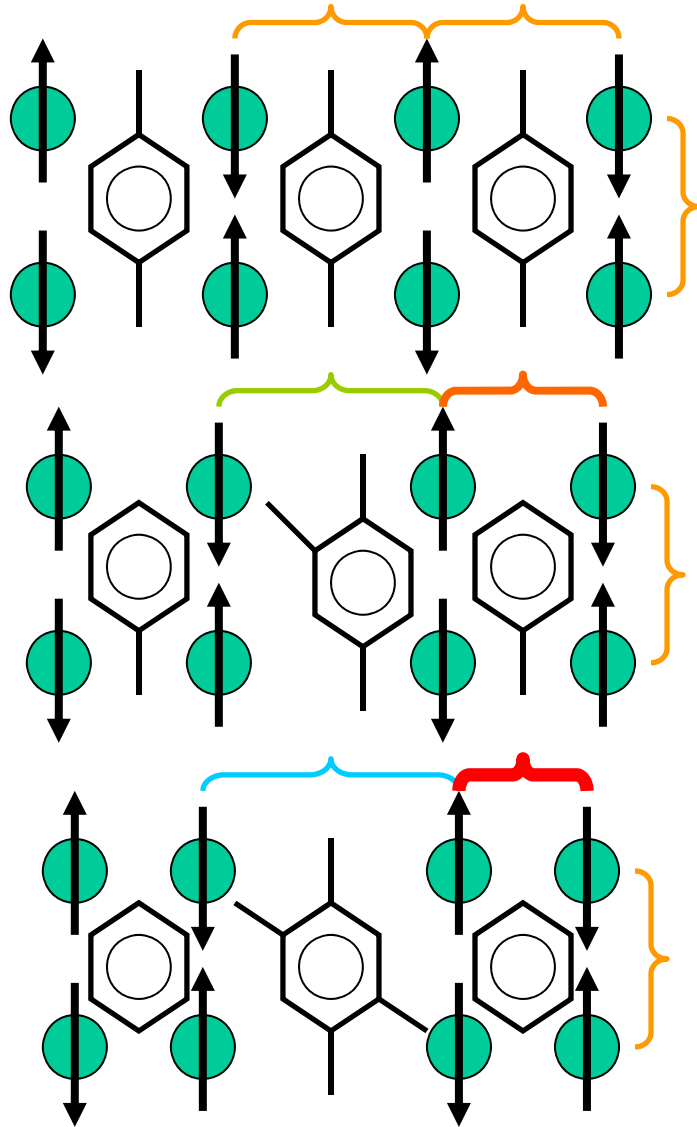
Rückblick auf Spindynamik

- Spindynamik ist Zeit- und Feldabhängig.
- AC-Suszeptometrie enthüllt wie schnell ein Spin auf ein äusseres Feld "antworten" kann – aufgeteilt in χ' (Realteil – "in Phase") und χ'' (Imaginärteil).
- Mit B-Feld erzwungene Spin-Flip und -Flop-Prozesse berichten über Spin-Spin-Kopplungen.
- AC und DC Suszeptibilität, kombiniert, helfen dabei exotische Spinzustände zu identifizieren oder gewisse Verunreinigungen auszuschliessen.





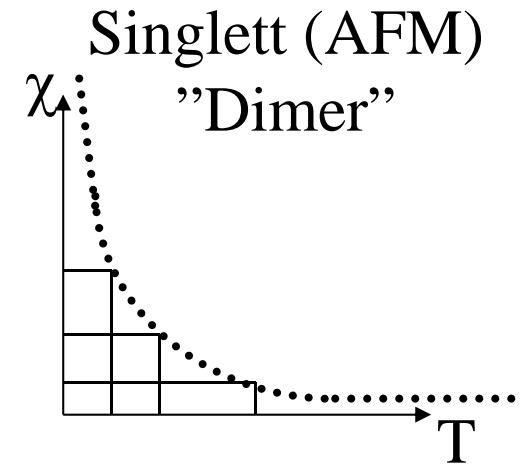
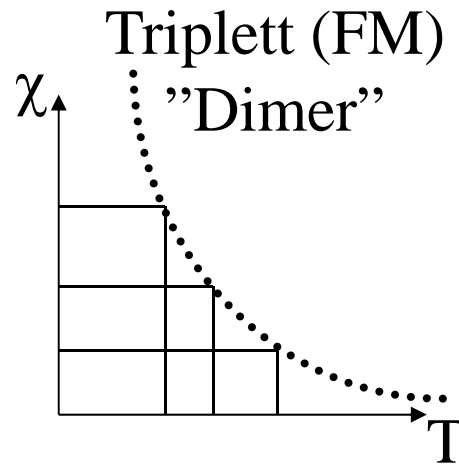
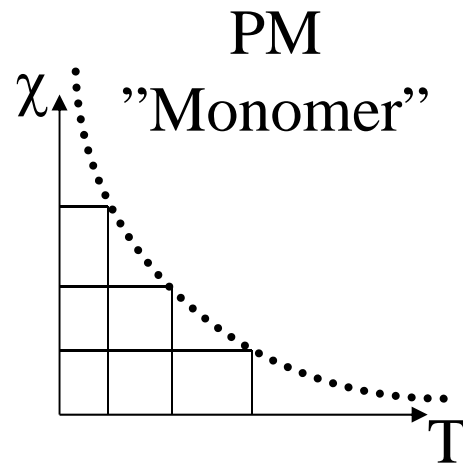
Monomer bis Dimer



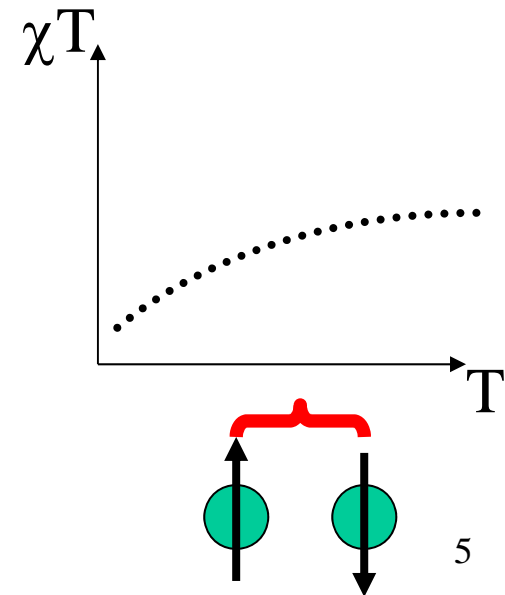
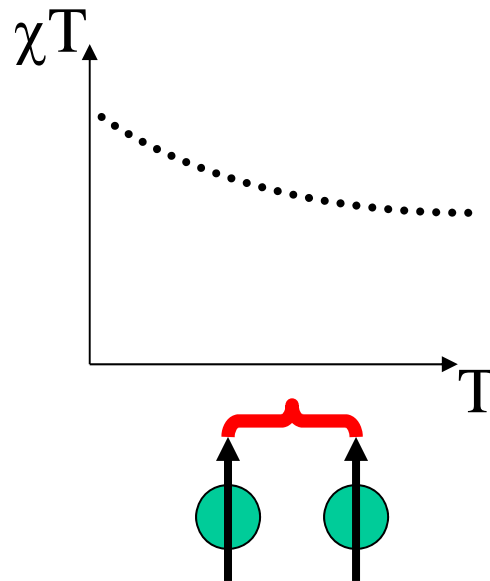
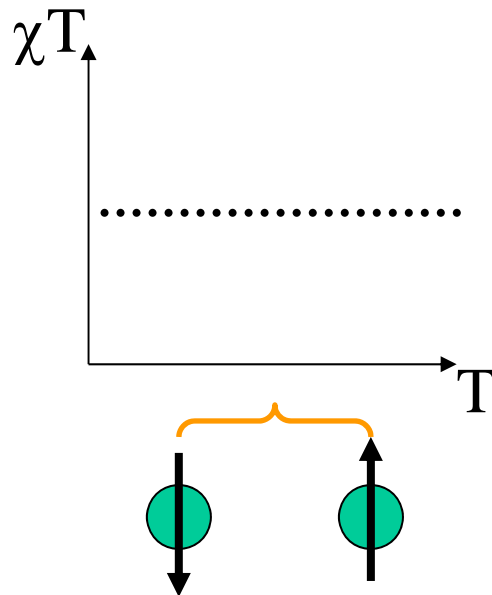
wird oft von der Struktur vorgegeben was möglich ist.

J ist hier die magnetische
Kopplungskonstante und
"unabhängig" von der Struktur

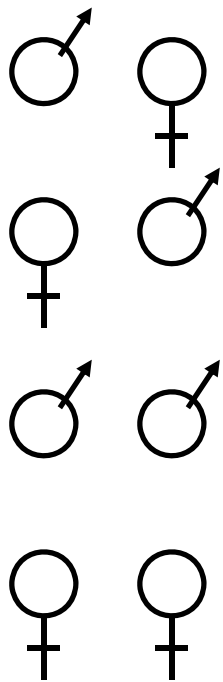
von χ bis χT



Wie würde eine $\chi^{-1}(T)$ Kurve aussehen?



Die Energie eines Pärchen



AFM		FM	
\uparrow^{+1}	\downarrow^{-1}	\uparrow^{+1}	\uparrow^{+1}
$S_i = 1$	$S_j = 1$	$S_i = 1$	$S_j = 1$
$H = J(S_i \cdot S_j)$			
$J/k_B = -X \text{ (K)}$		$J/k_B = +X \text{ (K)}$	
(Leider gibt es keine einheitliche Regel für + und -!)			

Im Gleichgewicht mit

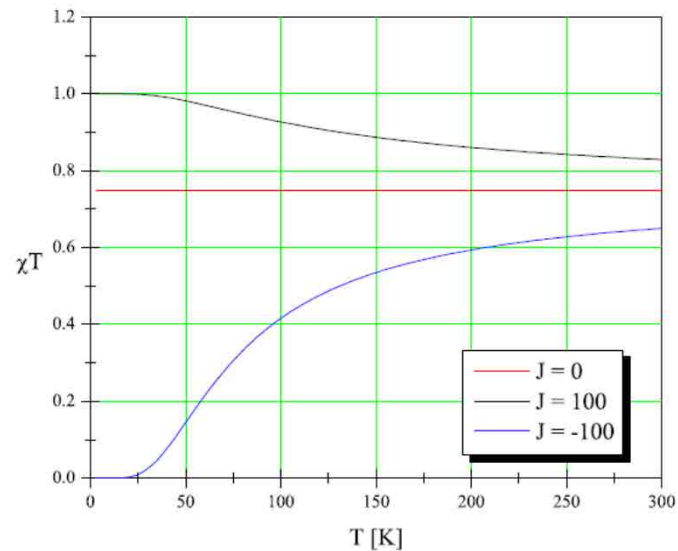
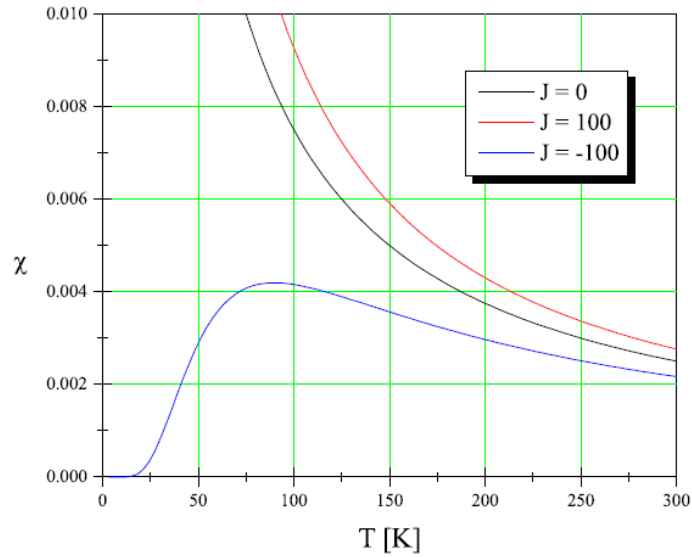
Temperatur
 $E = k_B \times T$

Spin im Feld
 $E = S \times g \times \mu_B \times B$

Wenn wir χ vergleichen kann das Feld (bei hohen Ts) abgekürzt werden.

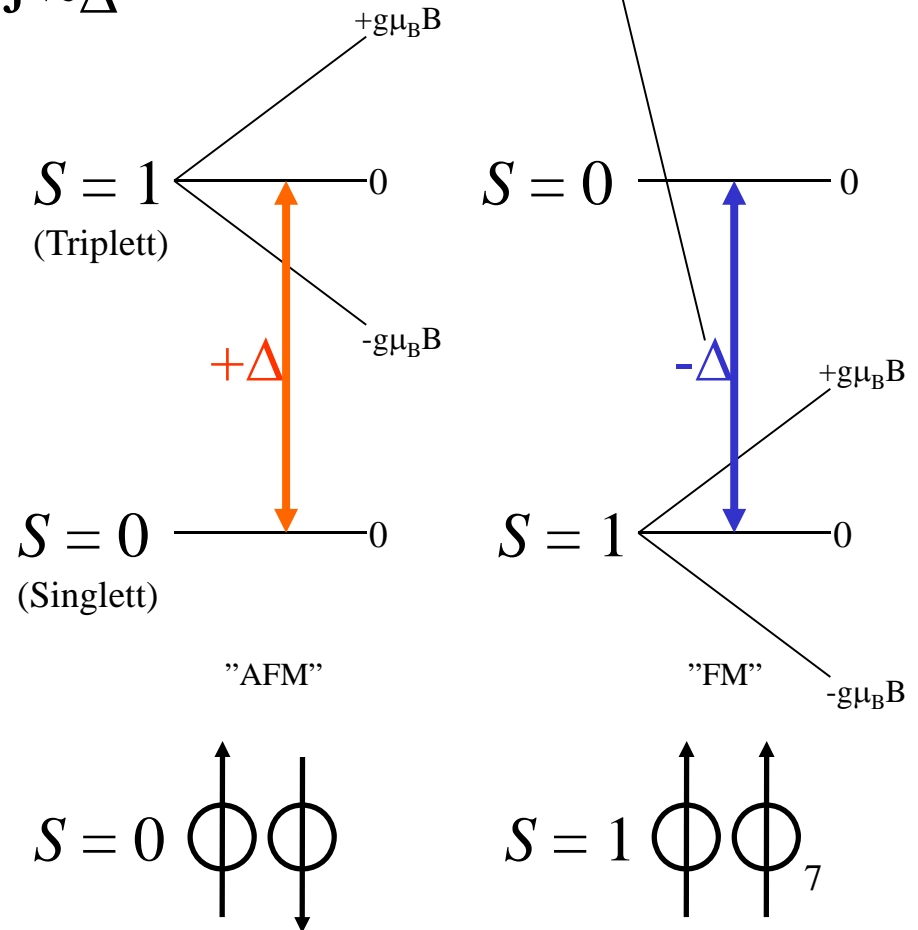
Dimer Modell

nach *Van-Vleck* und *Bleaney-Bowers*

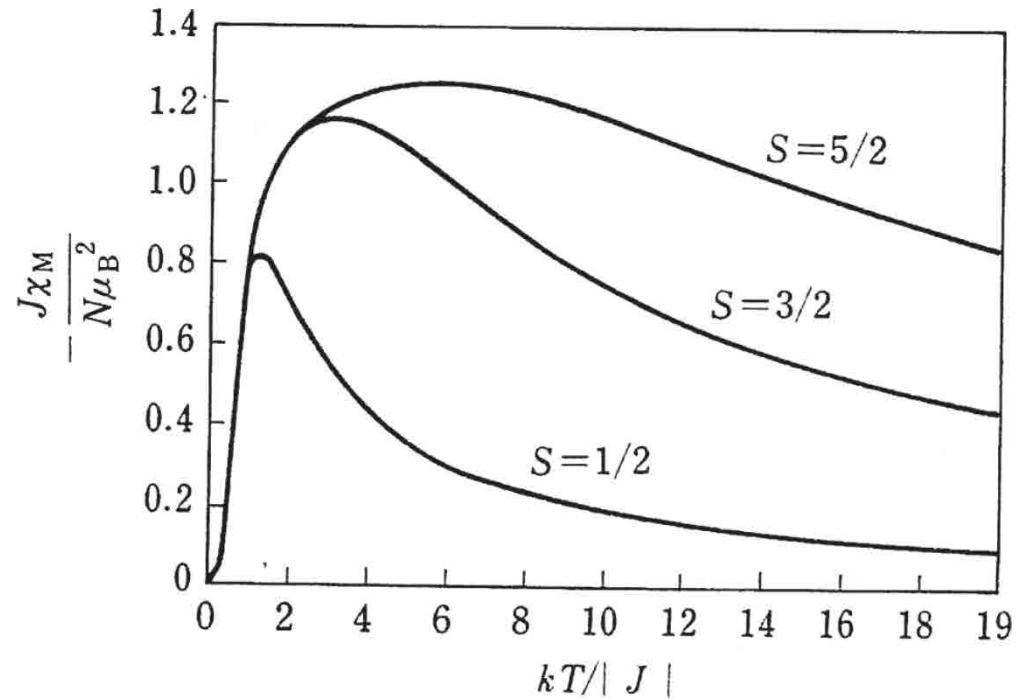


$$\chi = \frac{2Ng\mu_B^2}{k_B T (3 + e^{\Delta/k_B T})}$$

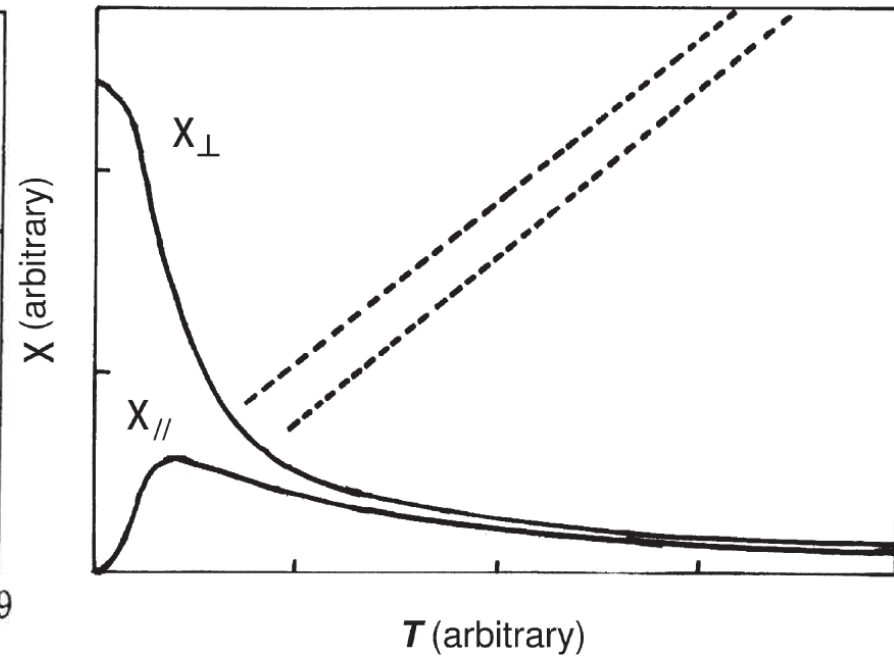
$J \sim \Delta$



Weitere Parameter bei Dimeren



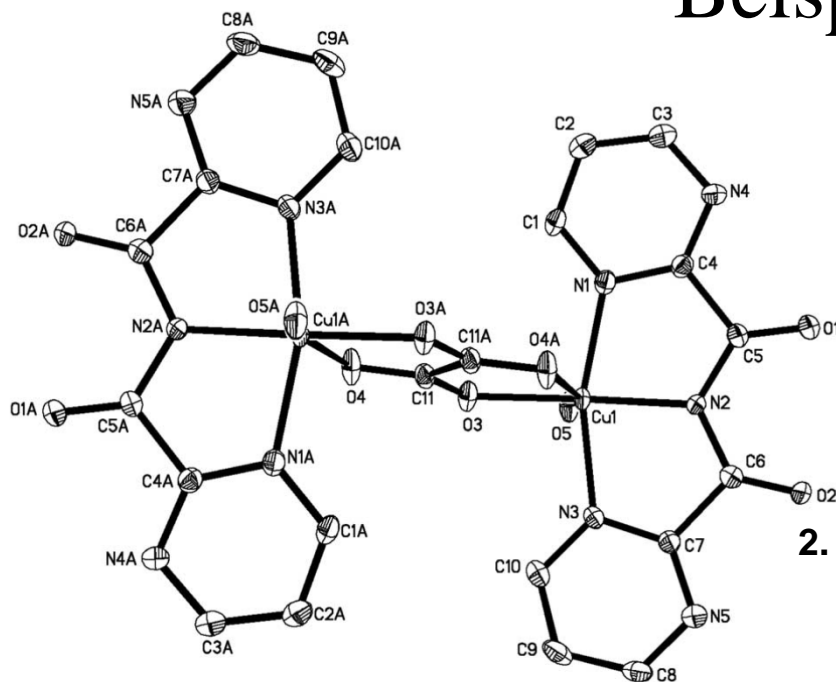
Die grösser der Spin hat einen Einfluss auf die Kurvenform



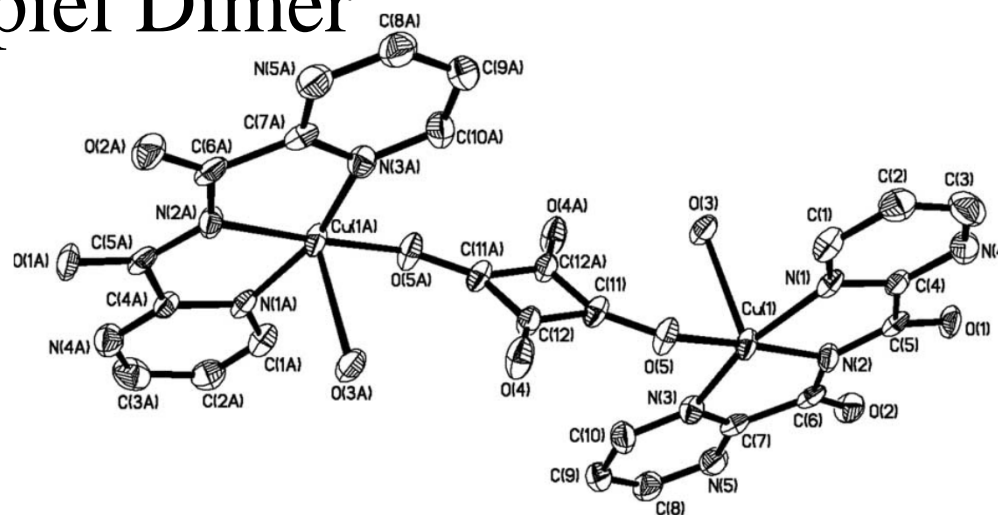
Wenn die Spins eines Dimers Anisotropie aufweisen, hat es eine Einwirkung auf χ .

D – für *Ising* spins
E – für *XY* spins

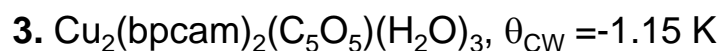
Beispiel Dimer



1. $[\text{Cu}_2(\text{bpcam})_2(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)]$, $J = +0.75 \text{ cm}^{-1}$, $g = 2.14$



2. $[\text{Cu}_2(\text{bpcam})_2(\text{H}_2\text{O})_4(\text{C}_4\text{O}_4)] \times 10\text{H}_2\text{O}$, $J = +1.26 \text{ cm}^{-1}$, $g = 2.10$



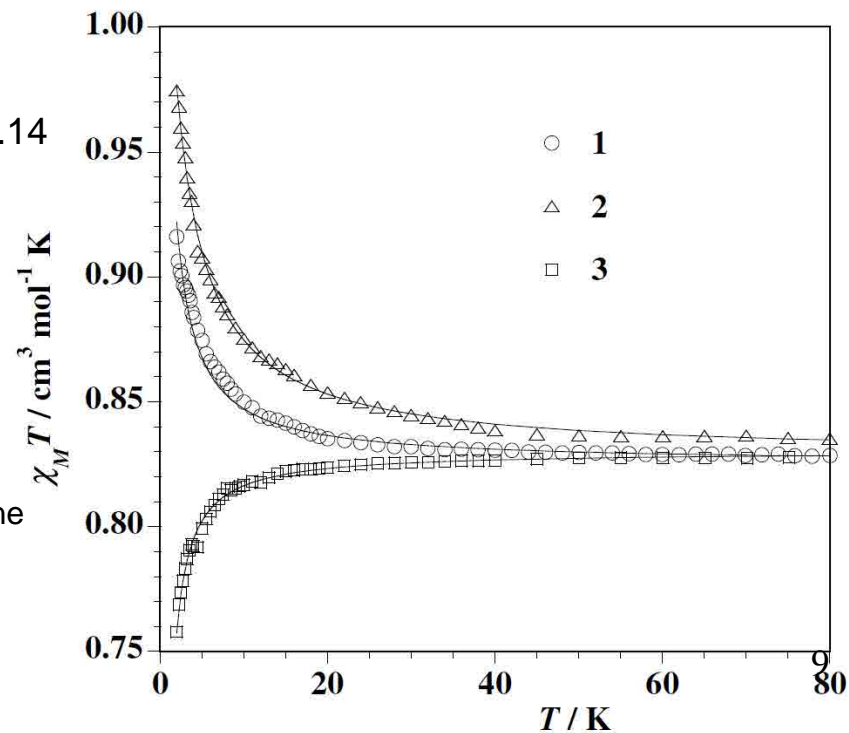
bpcam = bis(2-pyrimidyl)amidate

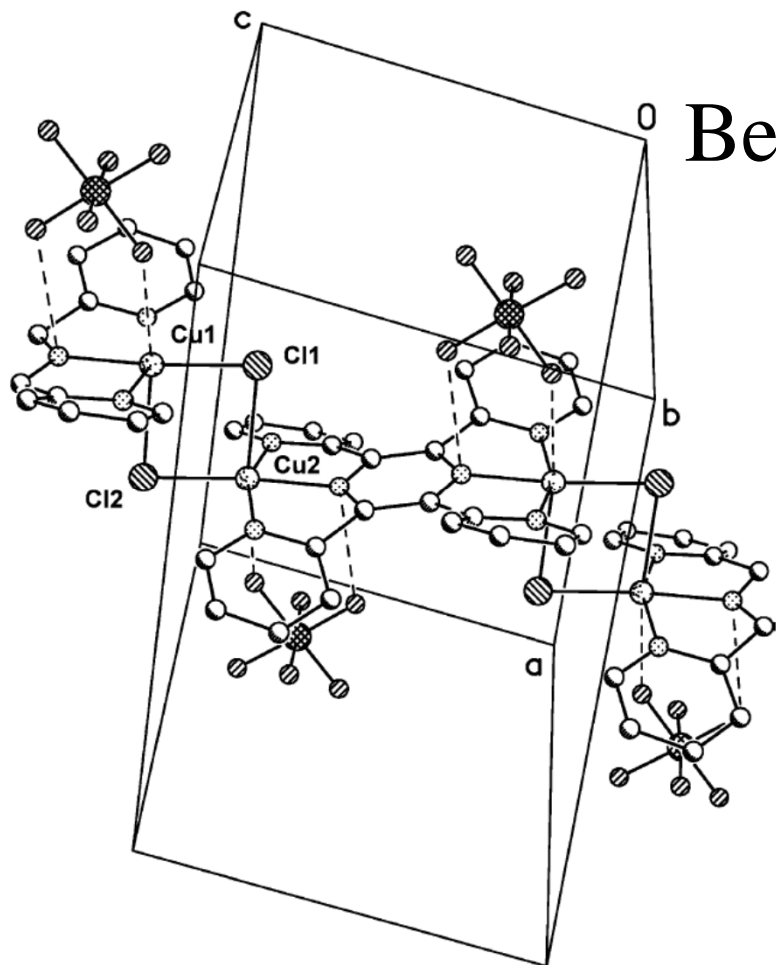
$\text{C}_2\text{O}_4^{2-}$ = dianion of oxalic acid

$\text{C}_4\text{O}_4^{2-}$ = dianion of 3,4-dihydroxycyclobut-3-ene-1,2-dione

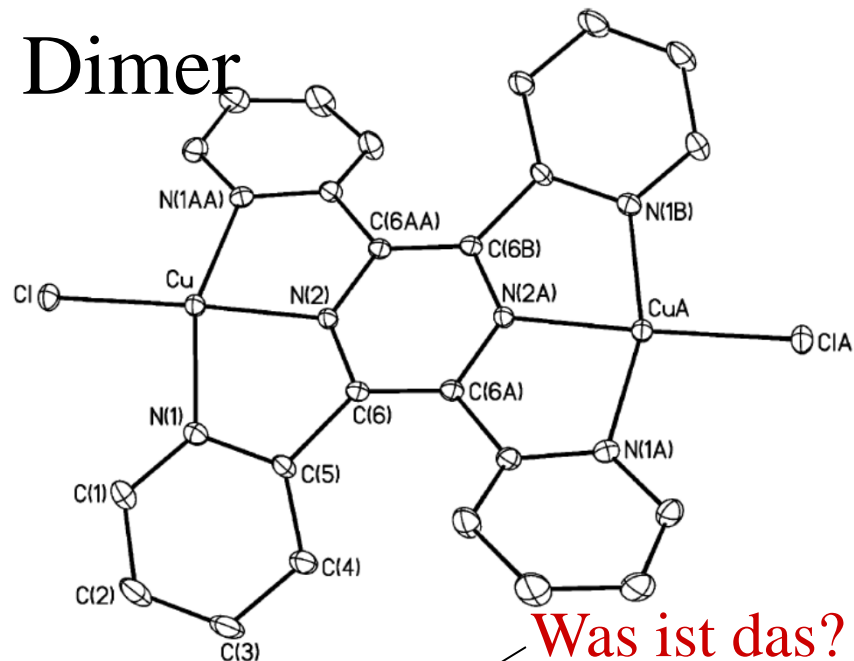
$\text{C}_5\text{O}_5^{2-}$ = dianion of 4,5-dihydroxy-cyclopent-4-ene-1,2,3-trione

$$H = J(S_i \cdot S_j)$$





Beispiel Dimer

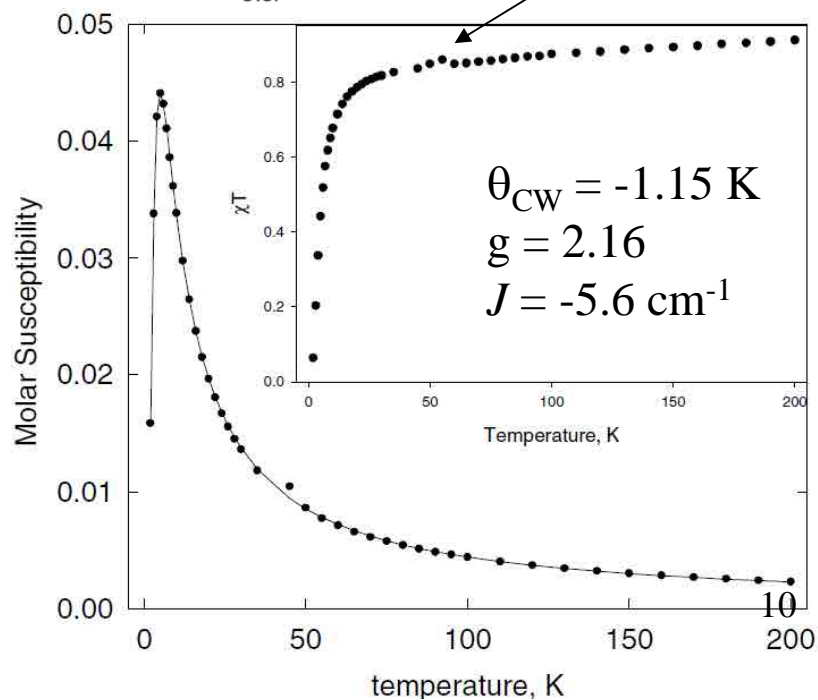


Was ist das?

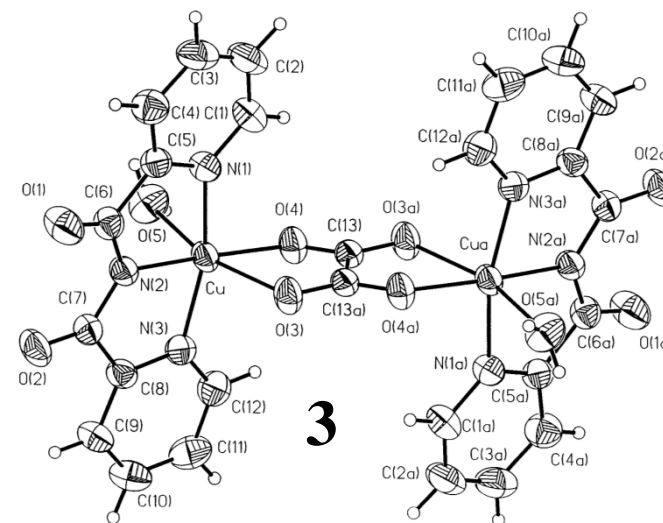
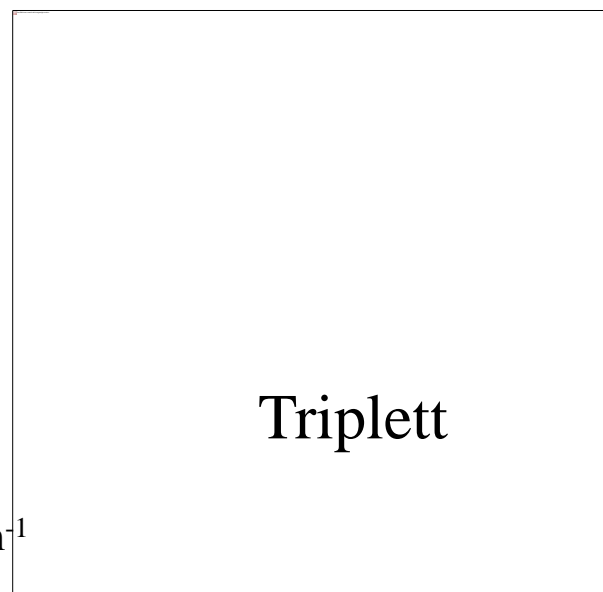
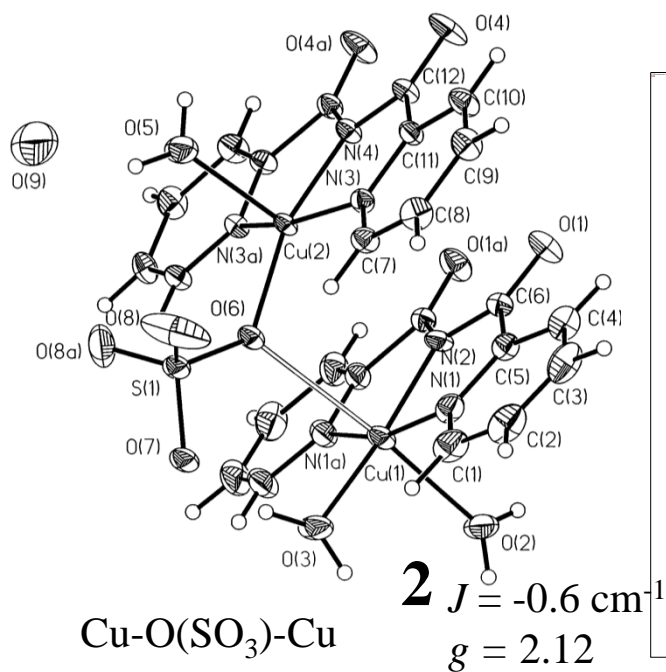
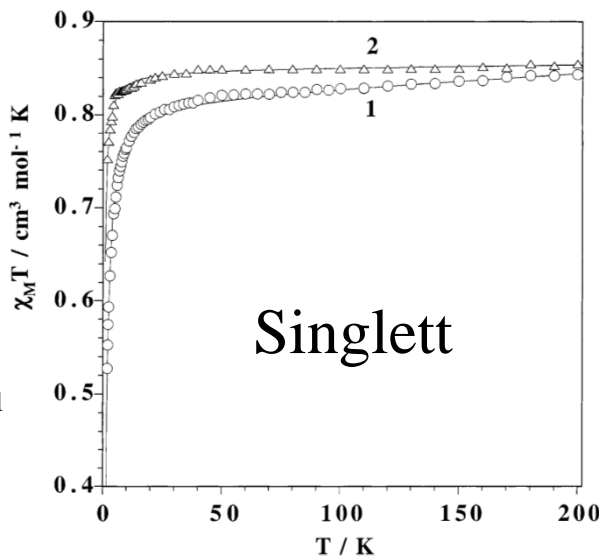
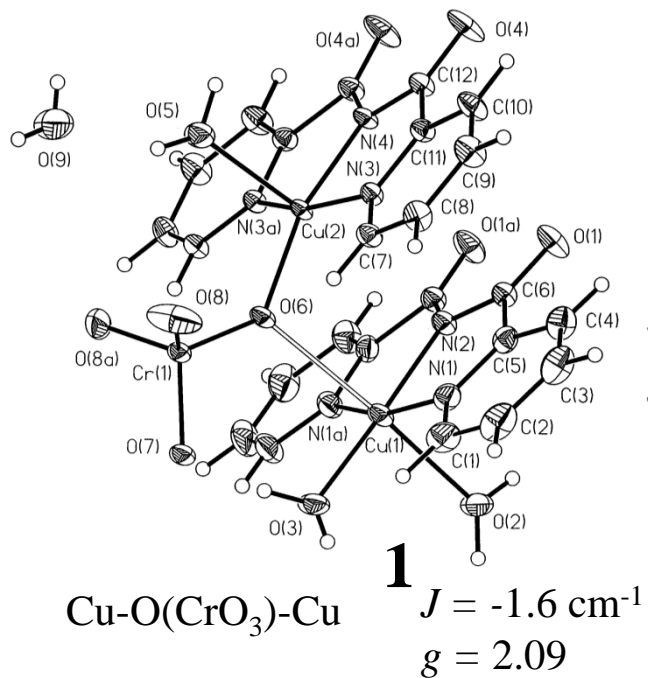
$[\{\text{CuCl}\}_2(\mu\text{-tppz})][\text{PF}_6]_2$,
tppz = 2,3,5,6-tetra-2-pyridinylpyrazin

$$\chi_m = \frac{C}{(T - \theta_{CW})} + \frac{(2Ng^2\mu_B^2/3k_B T)}{1 + (1/3)e^{(-2J/k_B T)}} + \chi_0$$

2 Superaustausch-Pfade möglich
- die sind unterschiedlich!



Beispiel Dimer



Eine Demonstration

JulX, v1.4.1 (2008)

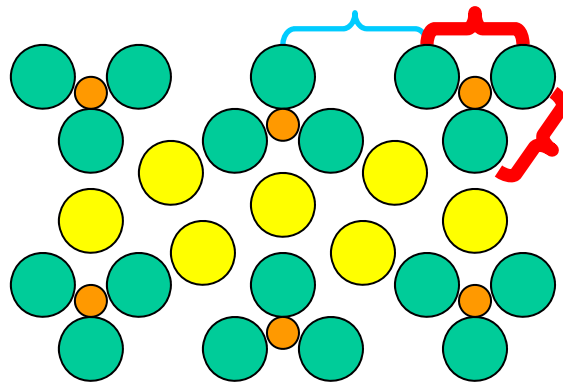
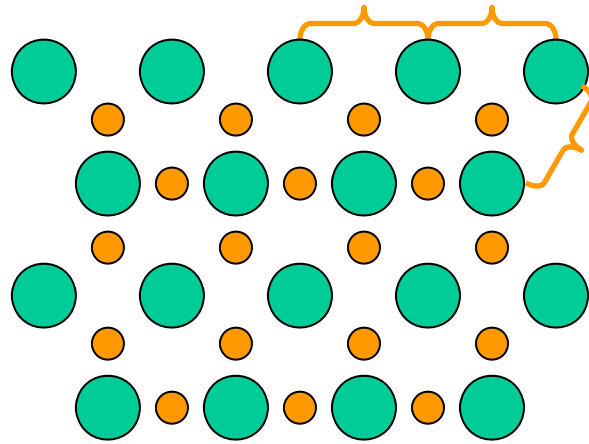
Eckhard Bill, MPI for Bioinorganic Chemistry, D-45470 Mülheim/Ruhr

ET1 – Cu-Dimer – Singlett ($m = 21.25$ mg, $M = 800.1$ g/mol)

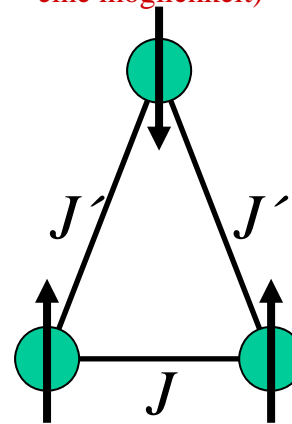
FEIIDMOX – Fe ($S=2$) –Dimer - Singlett

GF57sub – Fe ($S=5/2$) –Dimer - Triplett

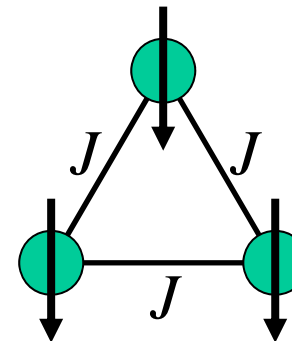
Monomer bis Trimer



FM, AFM
(gibt es noch eine Möglichkeit)

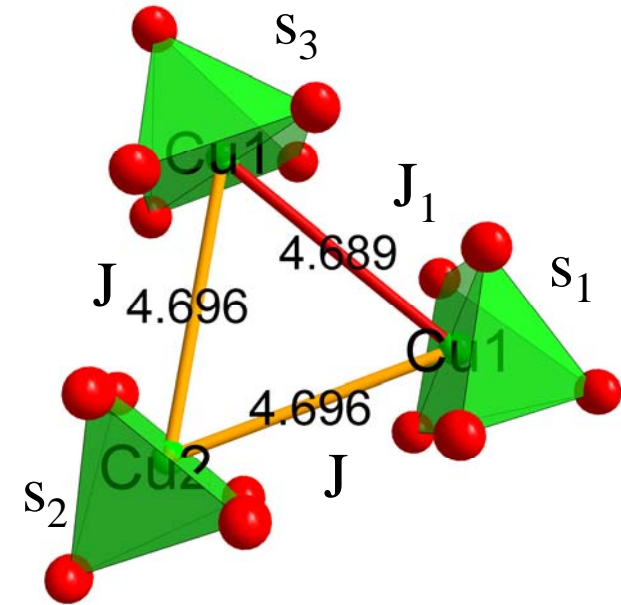
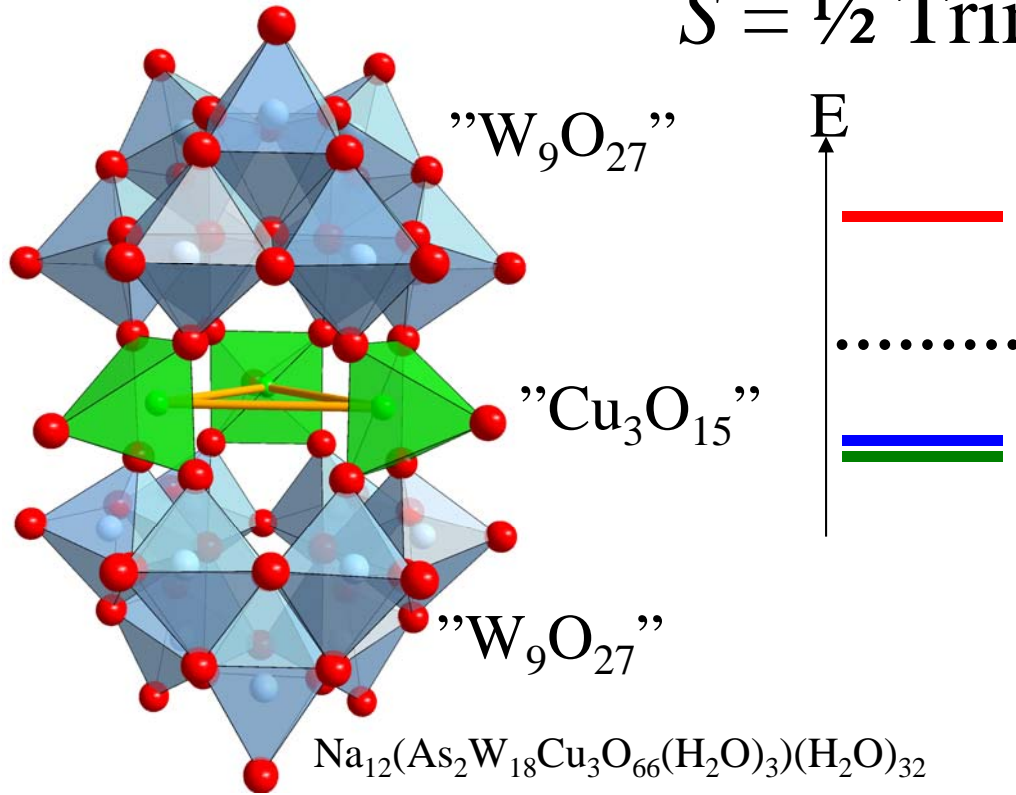


FM, AFM?



von der Struktur vorgegeben

$S = 1/2$ Trimer



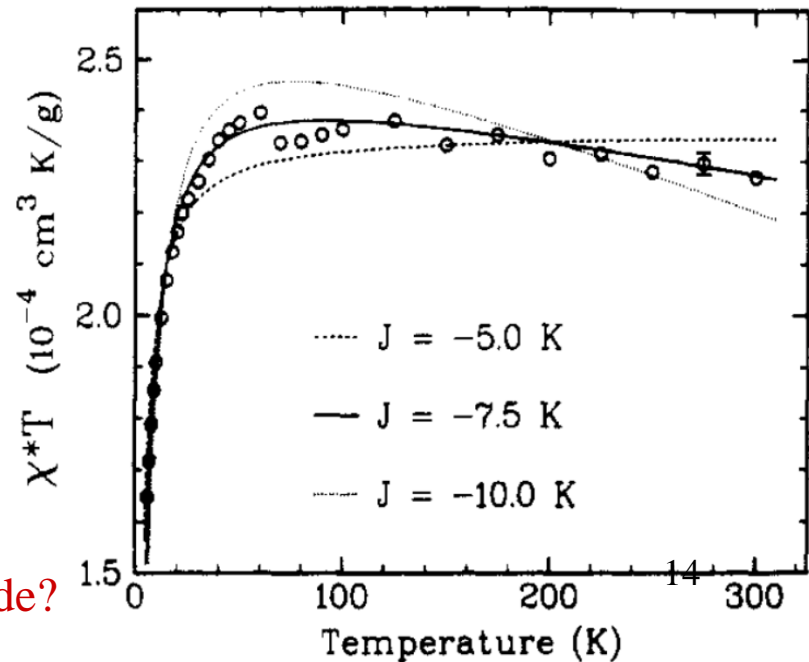
$$H = J(s_1 \cdot s_2 + s_2 \cdot s_3) + J_1(s_3 \cdot s_1)$$

$$\begin{array}{l}
 s_1 = \begin{array}{|c|c|} \hline +1/2 & -1/2 \\ \hline -1/2 & +1/2 \\ \hline \end{array} \begin{array}{|c|c|} \hline -1/2 & +1/2 \\ \hline +1/2 & -1/2 \\ \hline \end{array} \begin{array}{|c|c|} \hline +1/2 & -1/2 \\ \hline -1/2 & +1/2 \\ \hline \end{array} \\
 s_2 = \begin{array}{|c|c|} \hline +1/2 & -1/2 \\ \hline +1/2 & -1/2 \\ \hline \end{array} \begin{array}{|c|c|} \hline +1/2 & -1/2 \\ \hline -1/2 & +1/2 \\ \hline \end{array} \begin{array}{|c|c|} \hline -1/2 & +1/2 \\ \hline -1/2 & +1/2 \\ \hline \end{array} \\
 s_3 = \begin{array}{|c|c|} \hline +1/2 & -1/2 \\ \hline -1/2 & +1/2 \\ \hline \end{array} \begin{array}{|c|c|} \hline -1/2 & +1/2 \\ \hline -1/2 & +1/2 \\ \hline \end{array} \begin{array}{|c|c|} \hline -1/2 & +1/2 \\ \hline -1/2 & +1/2 \\ \hline \end{array}
 \end{array}$$

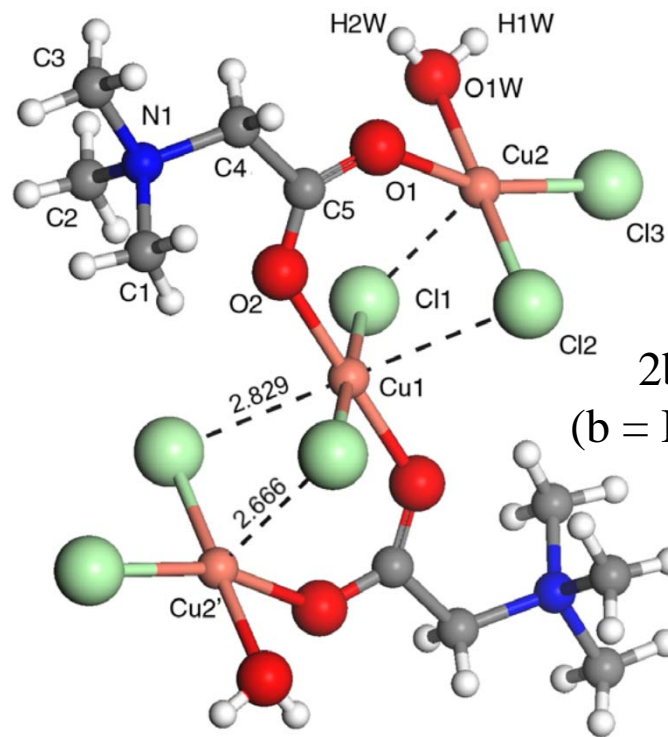
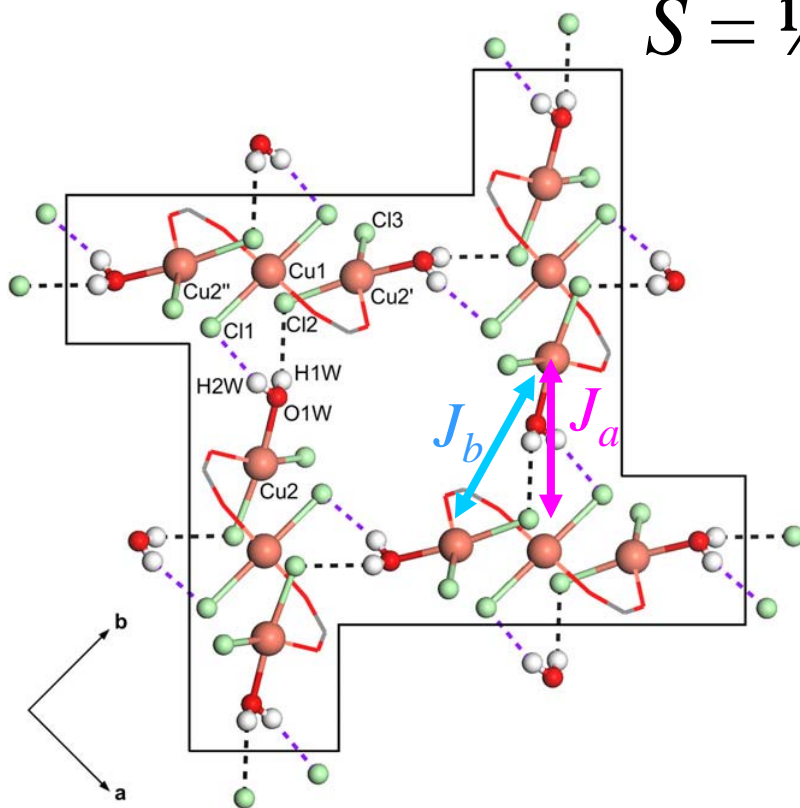
Wenn $J \approx J_1$
was passiert?

$$\begin{array}{l}
 (J/2) + (J_1/4) \qquad -3(J_1/4) \\
 -J + (J_1/4)
 \end{array}$$

Gibt es andere Zustände?

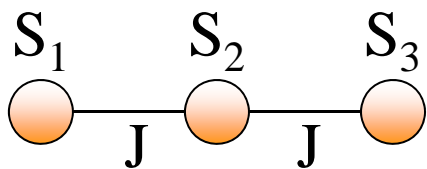


$S = 1/2$ gerades Trimer



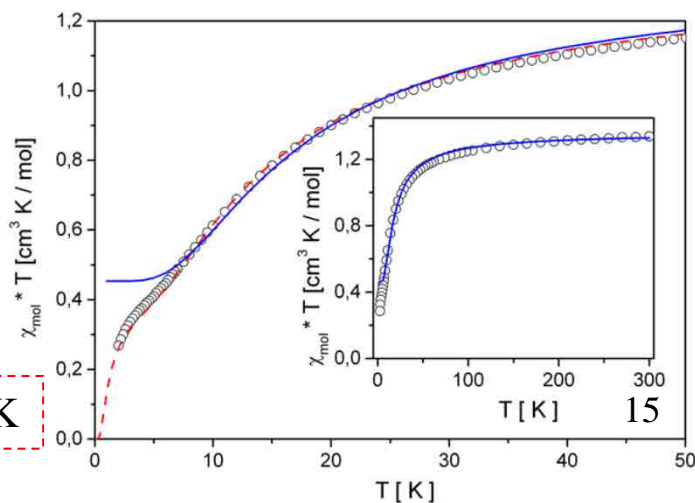
$2b \cdot 3\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$
($b = \text{Betain, C}_5\text{H}_{11}\text{NO}_2$)

$$H = -J(S_1S_2 + S_2S_3) - g\mu_B B(S_1 + S_2 + S_3)$$



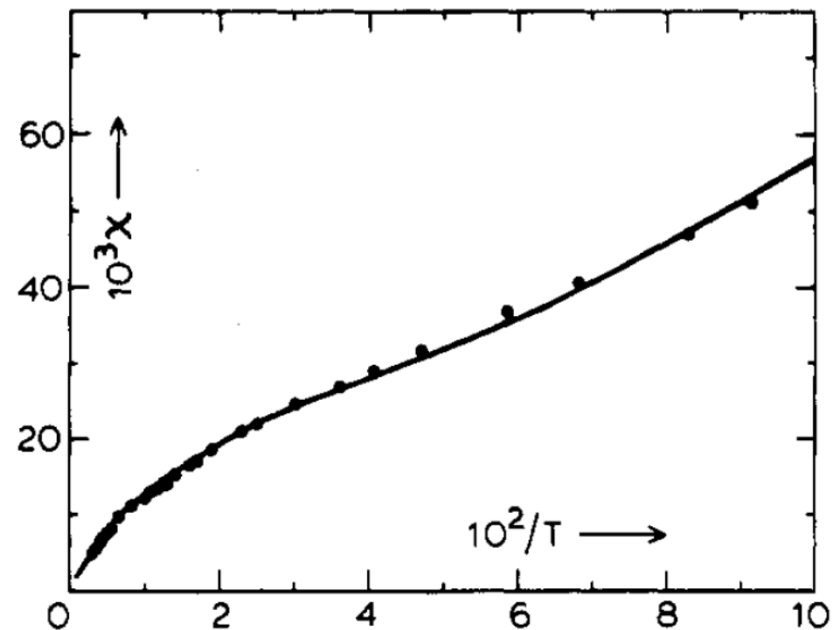
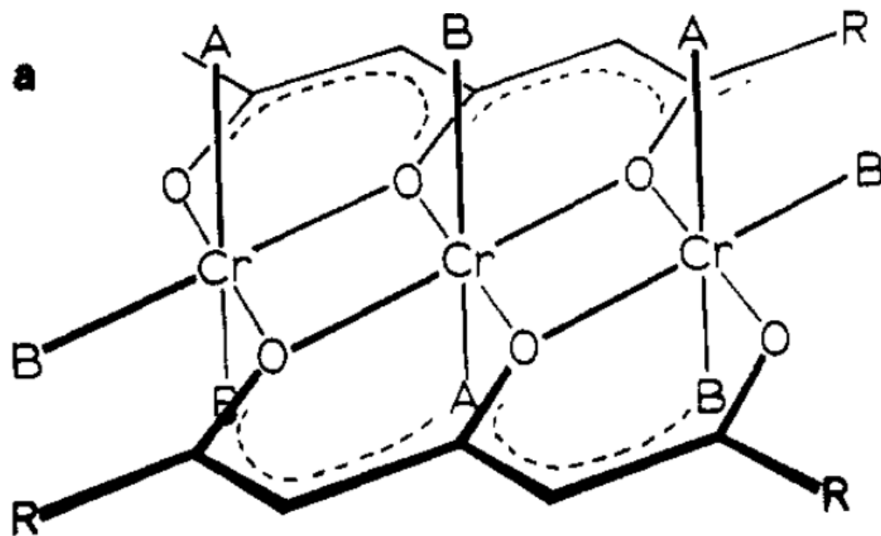
$$J/k_B = -20 \text{ K}$$

$$J/k_B = -15 \text{ K and } J_a/k_B = J_b/k_B = -4 \text{ K}$$



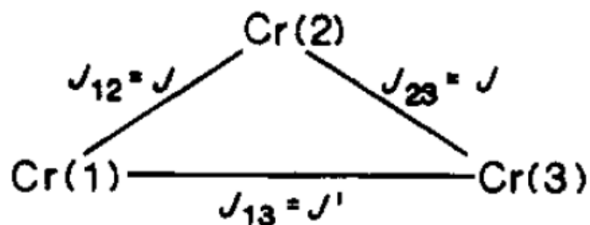
Komplexes Trimer ($S = 3/2$)

aber ohne Strukturangabe



$$H = -2(J_{12}S_1 \cdot S_2 + J_{23}S_2 \cdot S_3 + J_{13}S_1 \cdot S_3)$$

$$\chi = \frac{N\mu_B^2 g^2}{12k_B T} \frac{33A_1 + 21A_2 + 35A_3 + 5A_4 + A_5}{A_1 + A_2 + 3A_3 + A_4 + A_5}$$



$$J = -6.00 \text{ cm}^{-1}$$

$$J' = -1.35 \text{ cm}^{-1}$$

$$A_1 = 5x^{21}y^{12}$$

$$A_2 = 4x^{12}y^6(x^6+y^6)$$

$$A_3 = x^5(y^{12}+x^6y^6+x^{10}y^2)$$

$$A_4 = 2(y^{12}+x^6y^6+x^{10}y^2+x^{12})$$

$$A_5 = x^3y^2(y^4+x^4)$$

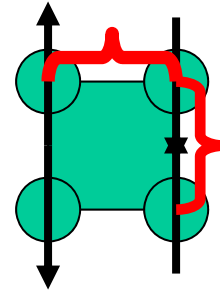
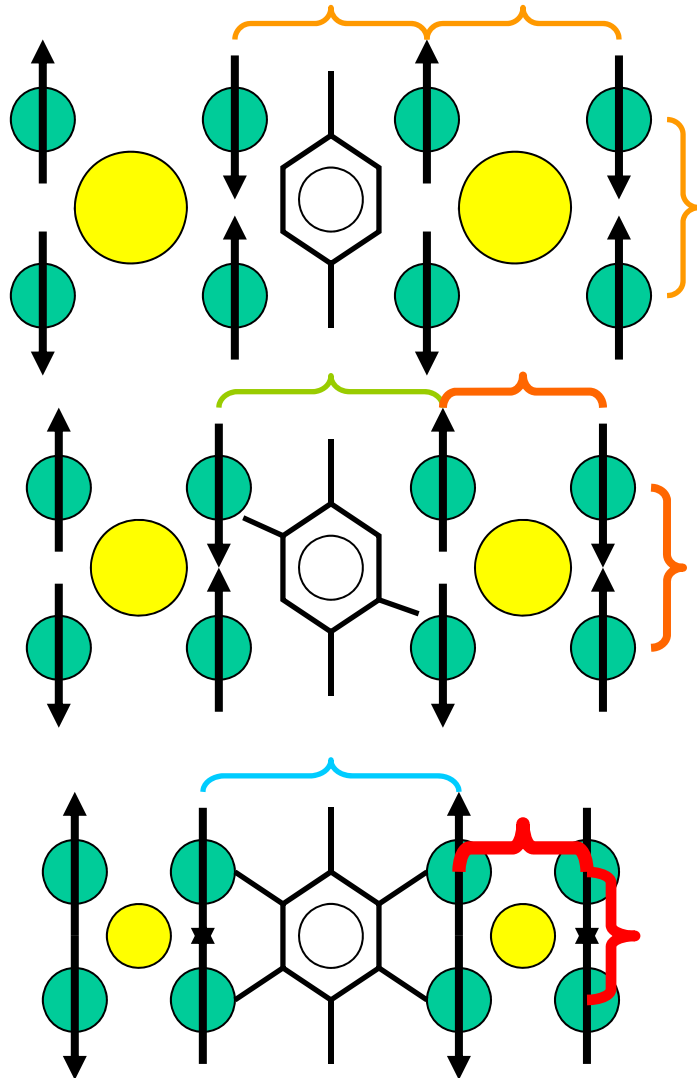
$$x = e^{2J/k_B T}$$

$$y = e^{2J'/k_B T}$$

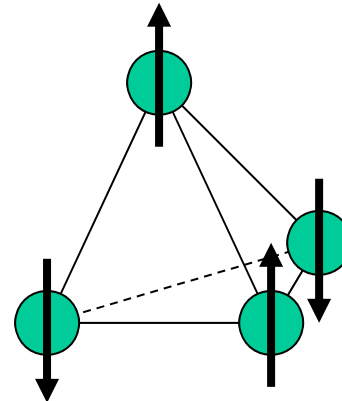
$\text{Cr}_3(\text{lig})_2(\text{H}_2\text{O})_3(\text{OH})_5$, lig = 1,5-diphenyl-1,3,5-pentanetrionato
- keine bekannte Struktur!

16

Monomer bis Tetramer



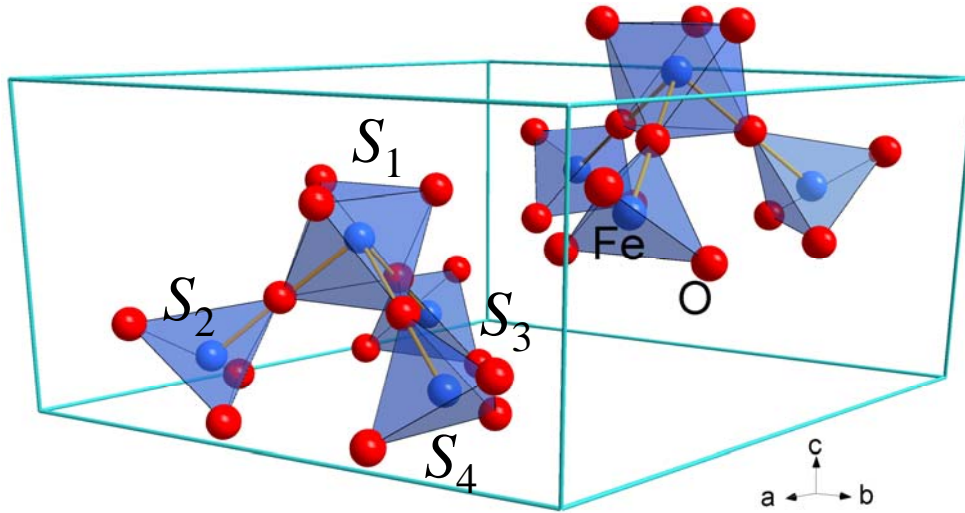
”FM, AFM”!



”FM”!, AFM”?

wird oft von der Struktur vorgegeben was möglich ist.

Fe-Tetramer in $\text{Ba}_6\text{La}_2\text{Fe}_4\text{O}_{15}$



$$H_{\text{ex}} = -2J_1(S_1S_2 + S_1S_3 + S_1S_4) - 2J_2(S_2S_3 + S_2S_4 + S_3S_4)$$

$$E(S_T, S') = -J_1 S_T(S_T + 1) + (J_1 - J_2)S'(S' + 1) + \text{constant}$$

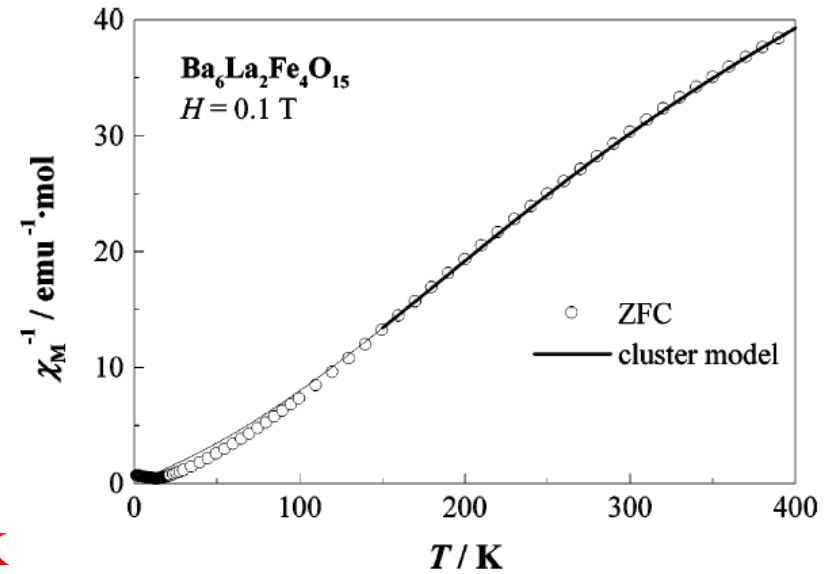
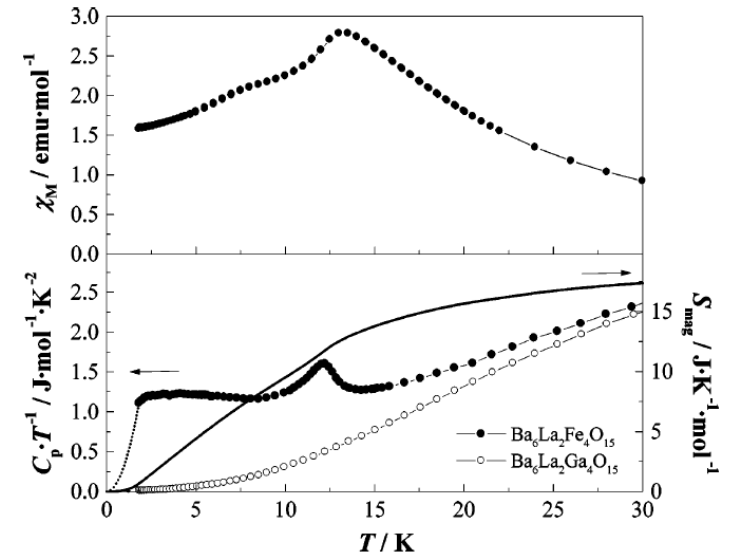
$$S_T = S_1 + S_2 + S_3 + S_4$$

$$S' = S_2 + S_3 + S_4$$

$$\chi_{\text{cluster}} = \frac{N_A g^2 \mu_B^2}{3k_B T} \frac{\sum_{S_T, S'} S_T(S_T + 1)(2S_T + 1) e^{-E(S_T, S')/k_B T}}{\sum_{S_T, S'} (2S_T + 1) e^{-E(S_T, S')/k_B T}}$$

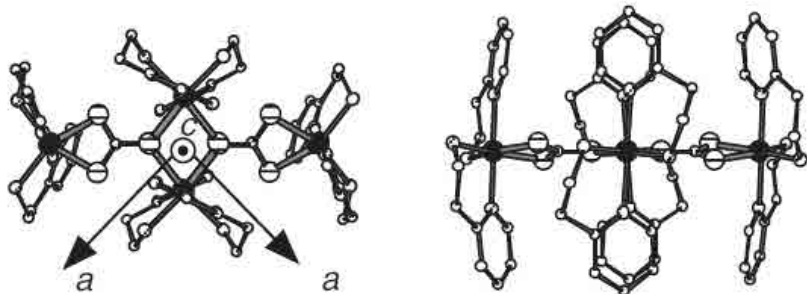
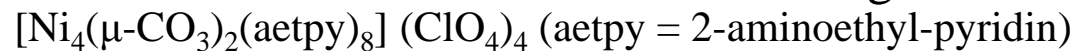
$$J_1 = -35.1(1) \text{ K}$$

$$J_2 = -3.41(2) \text{ K}$$



Ni-Tetramer

J_s aus Magnetisierung

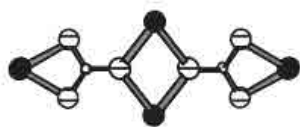


[0 0 1] projection

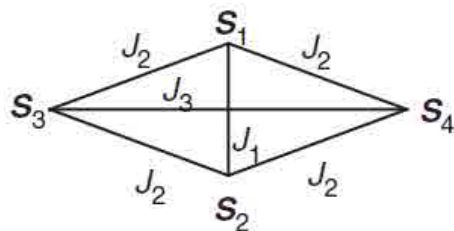
[1 1 0] projection

No magnetic order
($T = 0 \text{ K}$, $B = 0 \text{ T}$)

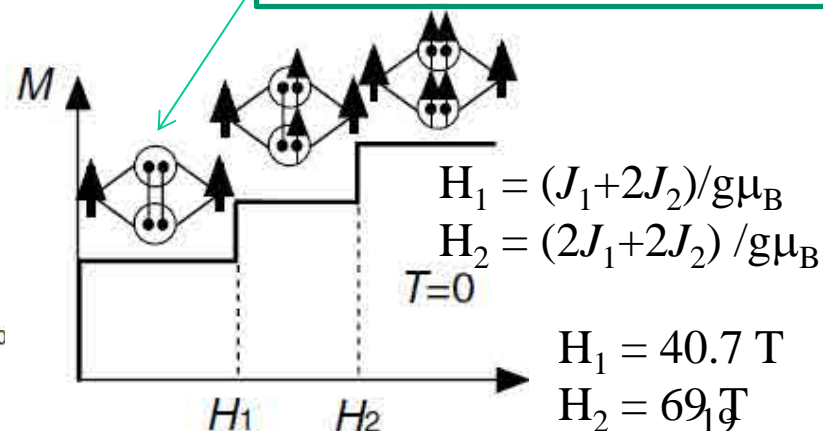
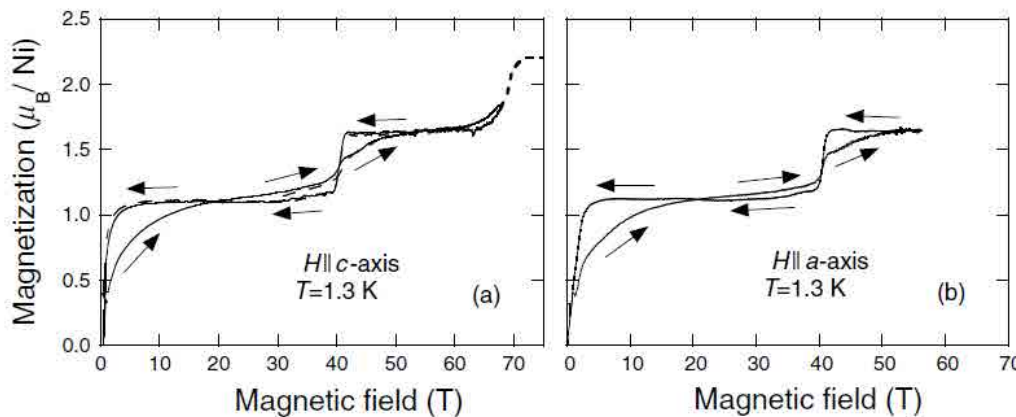
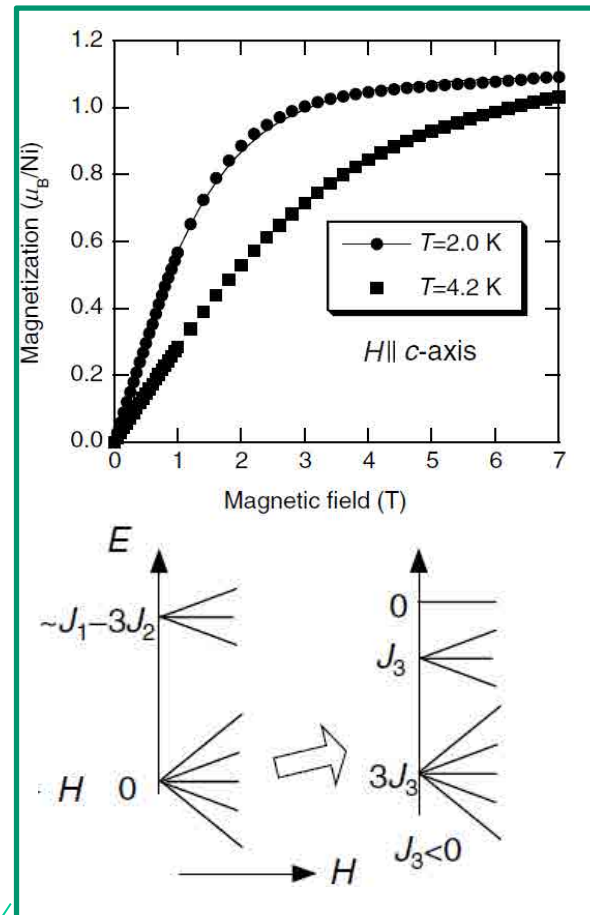
- Ni
- O
- C
- N



Framework

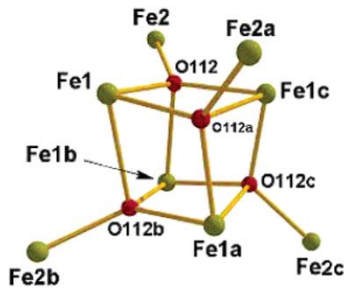
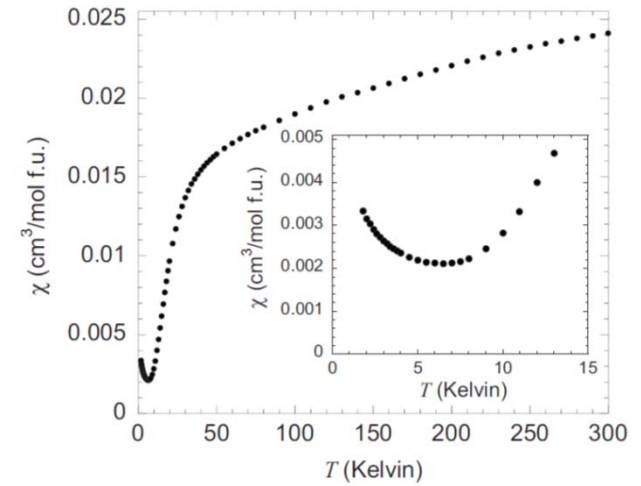
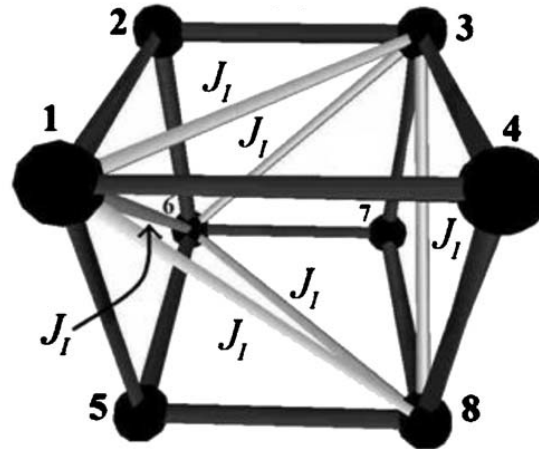
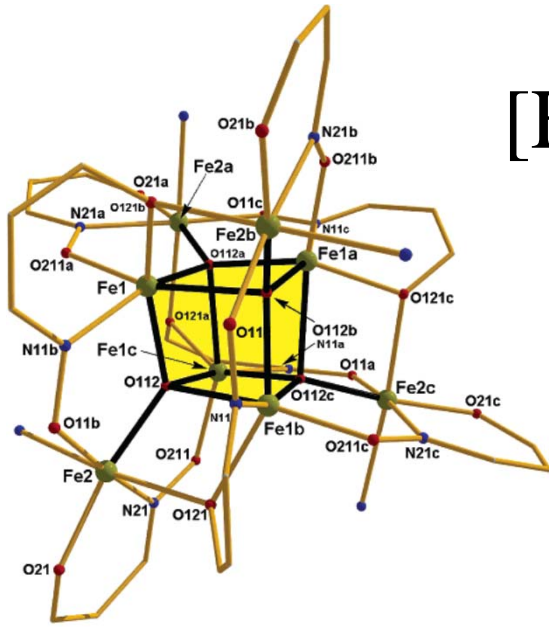


Angenommen:
 $J_1 > J_2 > 0 > J_3$
"AF" "FM"



$J_1/k_B = 49.7(5)$, $J_2/k_B = 9.3(2)$, $J_3/k_B = -0.63(2) \text{ K}$, $g = 2.229(2)$

[Fe₄O₄]-Kubus+4 Fe



$$\mathcal{H} = J_0(\vec{s}_1 \cdot \vec{s}_2 + \vec{s}_2 \cdot \vec{s}_3 + \vec{s}_3 \cdot \vec{s}_4 + \vec{s}_4 \cdot \vec{s}_1 + \vec{s}_5 \cdot \vec{s}_6 + \vec{s}_6 \cdot \vec{s}_7 + \vec{s}_7 \cdot \vec{s}_8 + \vec{s}_8 \cdot \vec{s}_5 + \vec{s}_1 \cdot \vec{s}_5 + \vec{s}_2 \cdot \vec{s}_6 + \vec{s}_3 \cdot \vec{s}_7 + \vec{s}_4 \cdot \vec{s}_8) + J_I(\vec{s}_1 \cdot \vec{s}_3 + \vec{s}_1 \cdot \vec{s}_6 + \vec{s}_1 \cdot \vec{s}_8 + \vec{s}_3 \cdot \vec{s}_6 + \vec{s}_3 \cdot \vec{s}_8 + \vec{s}_6 \cdot \vec{s}_8)$$

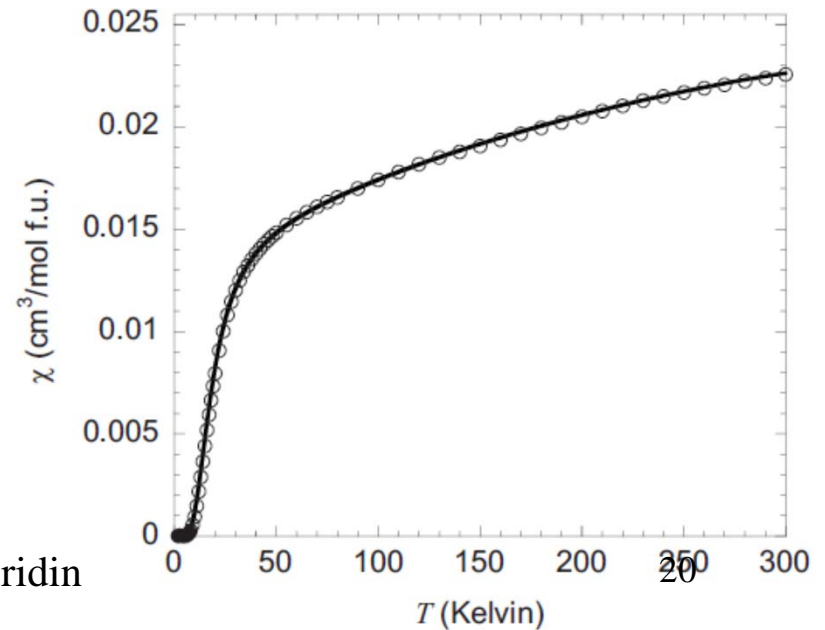
$$+ g\mu_B \vec{H} \cdot \sum_{i=1}^8 \vec{s}_i,$$

$$J_I = 22(2) \text{ K FM}$$

$$J_0 = 71(2) \text{ K}$$

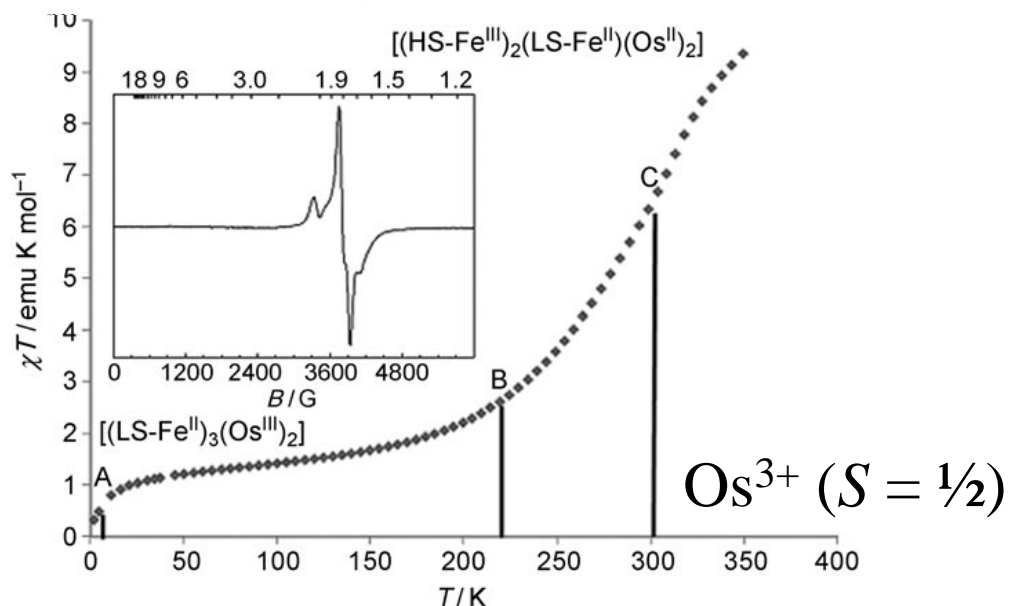
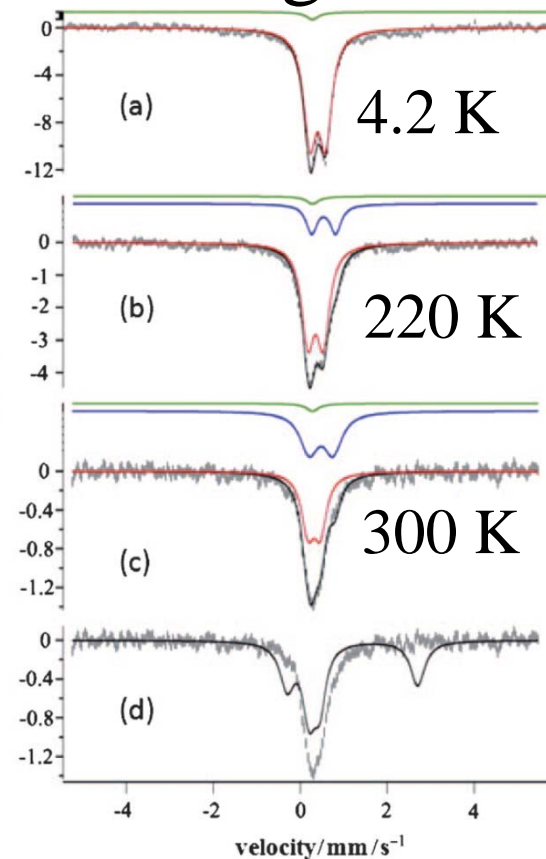
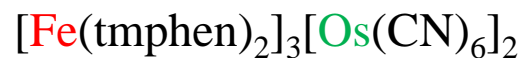
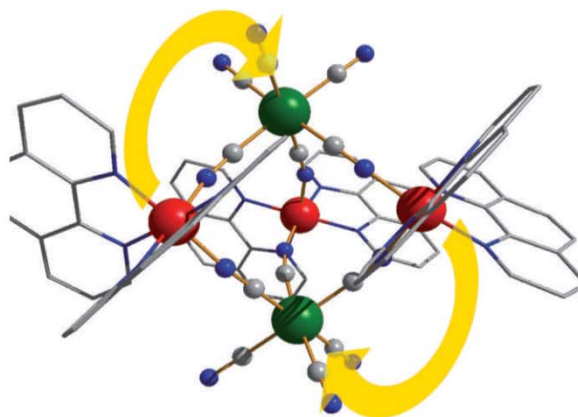
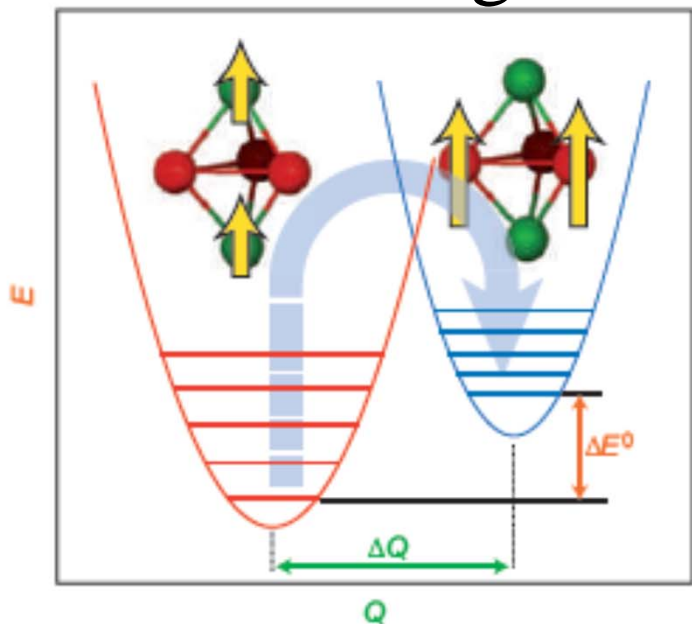


sao = salicylaldoxim – 2-hydroxybenzaldehyd oxim, py = pyridin



Zwei Sonderfälle

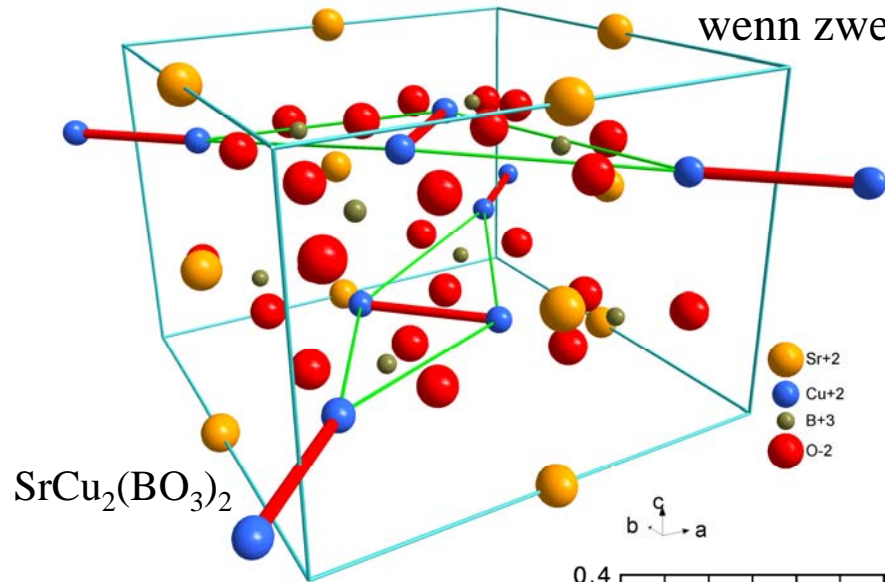
Ladung-Transfer Spin Zustandsänderung



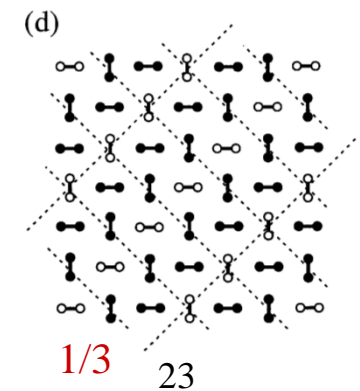
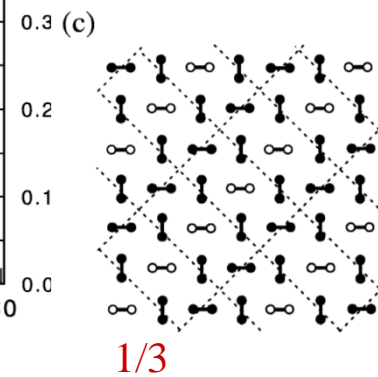
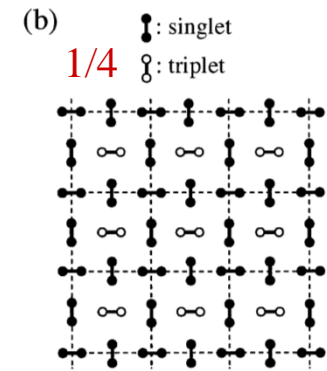
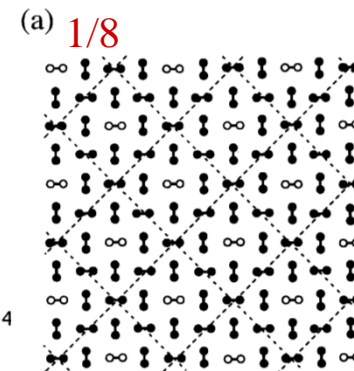
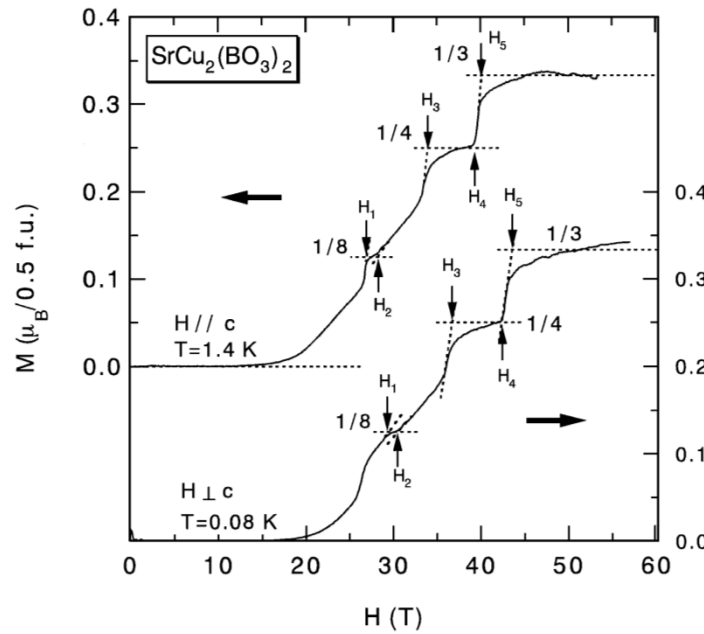
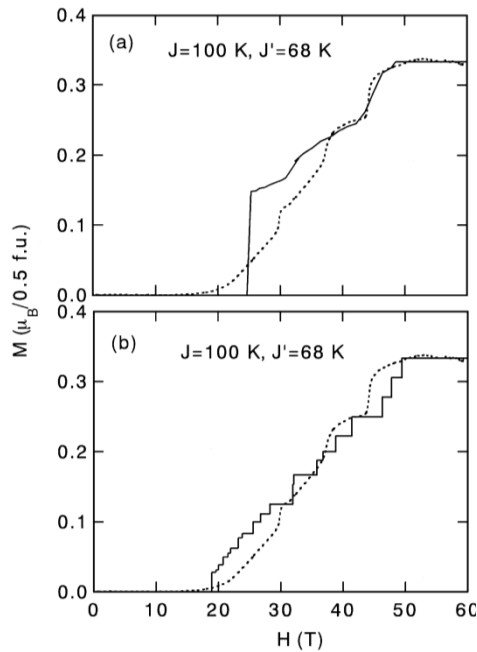
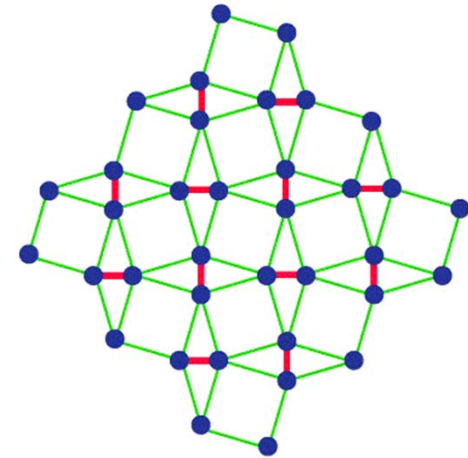
T [K]	Fe site	δ [mms ⁻¹] ^[a]	ΔE_Q [mm s ⁻¹]	Relative contribution [%]
4.2	LS Fe ^{II}	0.40	0.36	95
	LS Fe ^{II*}	0.28	0.00	5
220	LS Fe ^{II}	0.35	0.35	72
	HS Fe ^{III}	0.54	0.55	22
	LS Fe ^{II*}	0.28	0.00	6
300	LS Fe ^{II}	0.32	0.28	66
	HS Fe ^{II}	0.50	0.55	27
	LS Fe ^{II*}	0.28	0.00	6

Shastry Sutherland

wenn zwei Js konkurrieren



$J =$ —
 $J' =$ —



Zusammenfassung

- Auch ohne Spin-Ordnung können χ -Daten stark von Curie-Weiss-Verhalten abweichen.
- Wo Spin-Dimere oder -Polymere möglich sind gibt es auch WW. Ihre Stärke kann sehr unterschiedlich sein.
- Mittels Van-Vleck-Formel und eine gut überlegte Hamiltonian kann man eine χ -Temperatur anhängigkeit darstellen.
- Sobald magnetische Kopplungen auch zwischen den X-Meren entsteht wird alles natürlich noch komplizierter und langreichweitige Ordnung ist gut möglich.

Nächster Termin 15.6.2016 Magnetismus–Struktur