Spin-crossover phenomena of a Jahn-Teller active Mn(III) complex [Mn(taa)]

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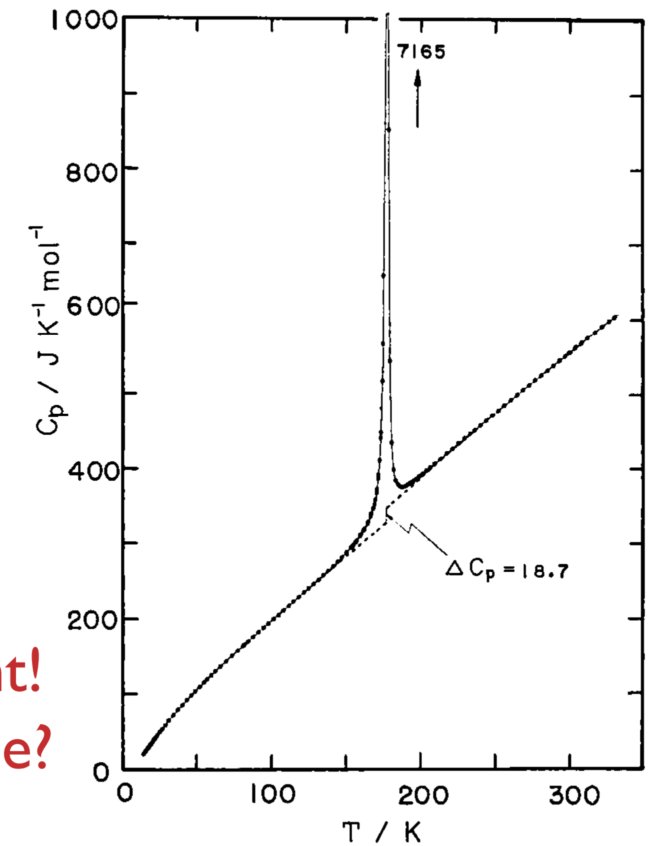
Milestone paper on SCO phenomena

PHONON COUPLED COOPERATIVE LOW-SPIN $^1A_1 \rightleftharpoons$ HIGH-SPIN $^5T_2$ TRANSITION IN $[Fe(phen)_2(NCS)_2]$ AND $[Fe(phen)_2(NCSe)_2]$ CRYSTALS

M. Sorai and S. Seki
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

(*Received* 5 *July* 1973)

J. Phys. Chem. Solids, 1974, Vol. 35, pp. 555–570.



$\Delta_{trs}S$ = 48.8 J K^{-1} mol^{-1}
>> *R* ln 5 (13.4 J K^{-1} mol^{-1})

Pure spin entropy is not sufficient!
Where is another entropy source?

→ Vibrational contribution

Central Dogma in thermally-driven SCO

- Entropy difference between HS and LS is dominated by vibrational contribution.
- Totally-symmetric breathing mode is important.

Spin-crossover temperature

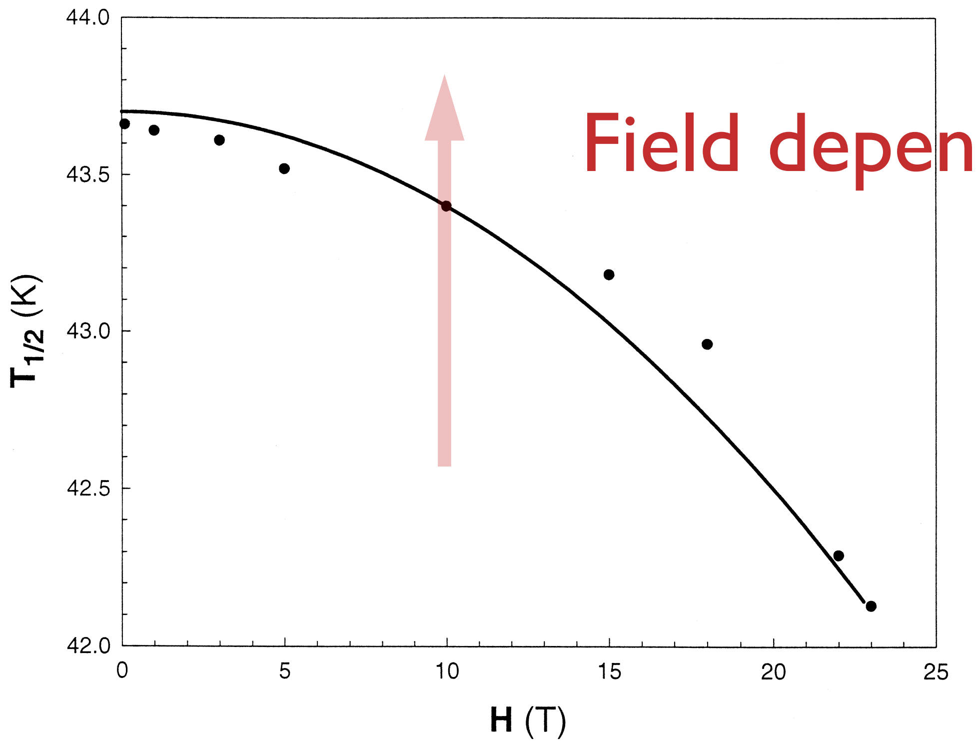
$$T_{1/2} = \Delta_{trs}H \,/\, \Delta_{trs}S$$

Field-induced SCO in [Mn^{III}(taa)]

The effect of a magnetic field on the inversion temperature of a spin crossover compound revisited

Yann Garcia [a], Olivier Kahn [a], Jean-Pierre Ader [b,*], Alexandre Buzdin [b], Yann Meurdesoif [b], Maurice Guillot [c]

Physics Letters A 271 (2000) 145–154



Field dependence of $T_{1/2}$

Field-induced SCO in [Mn^{III}(taa)]

The effe

Yann

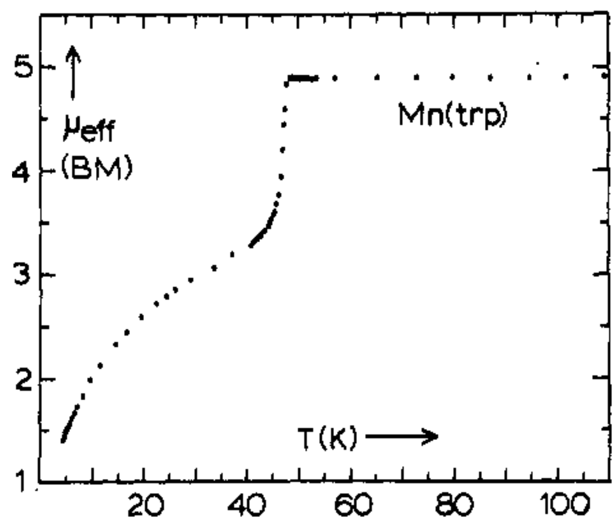
5–154

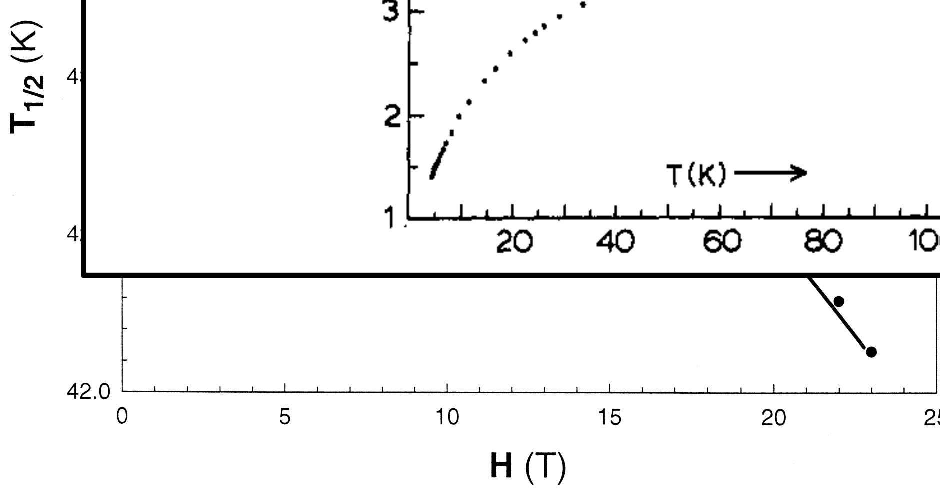
$T_{1/2}$

First Manganese(III) Spin Crossover and First d^4 Crossover. Comment on Cytochrome Oxidase

P. Greig Sim and Ekk Sinn*

J. Am. Chem. Soc. **1981**, *103*, 241–243





Field-induced SCO in $[Mn^{III}(taa)]$

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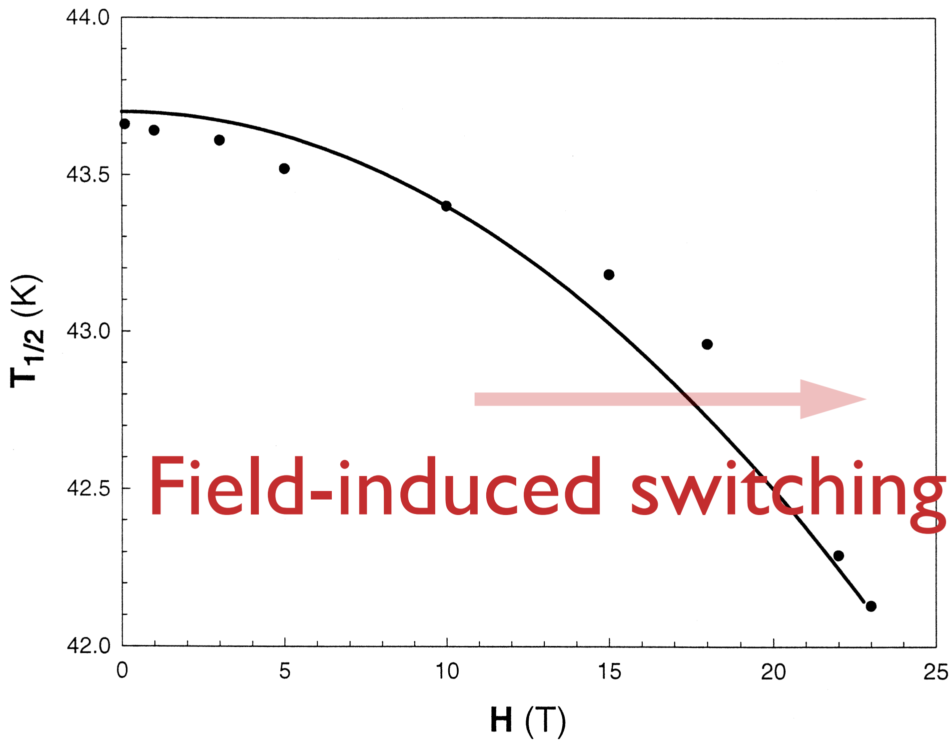
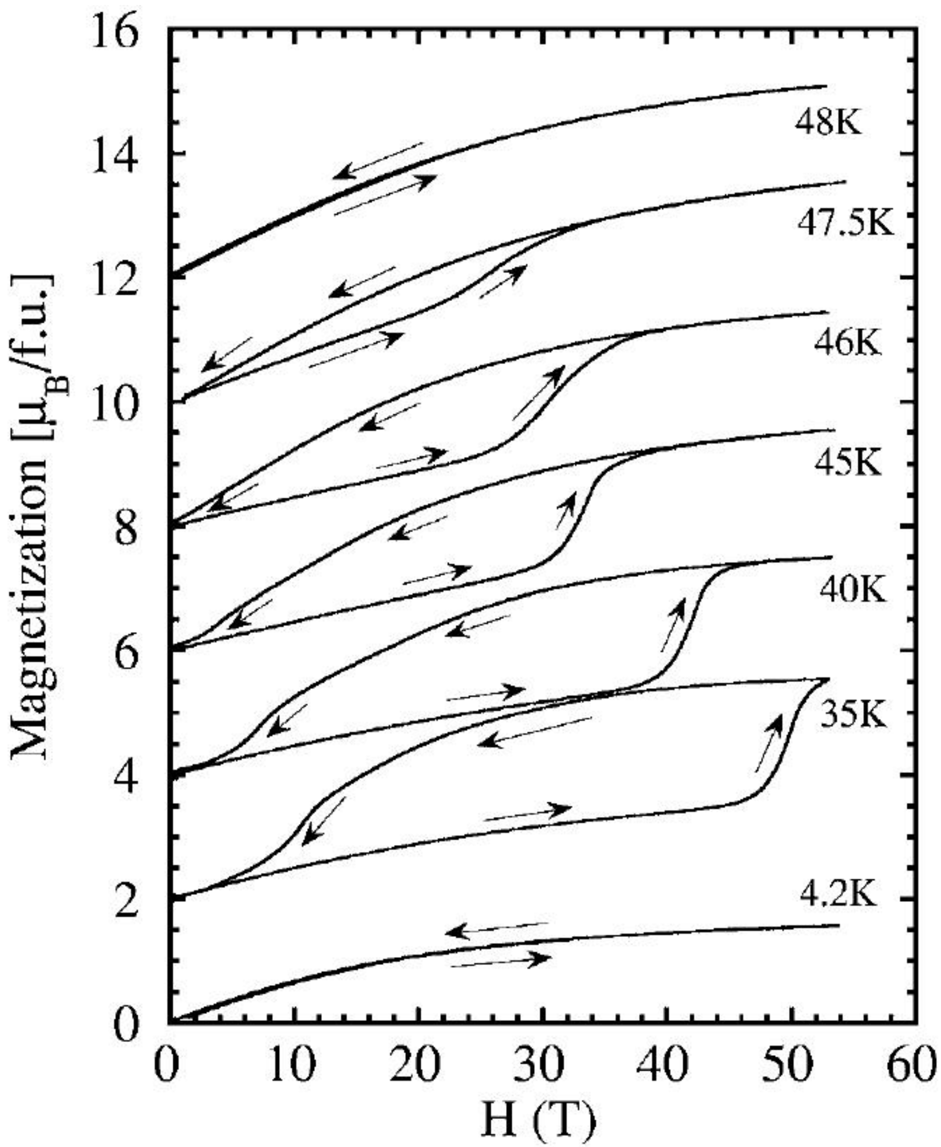
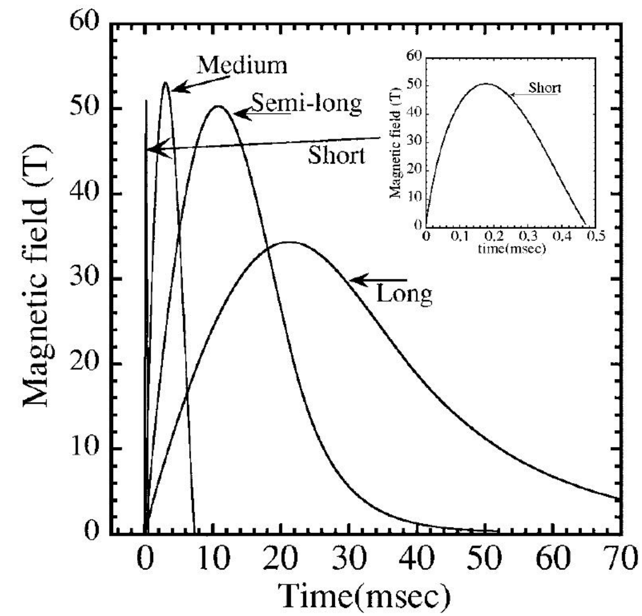


Field-induced switching from LS to HS

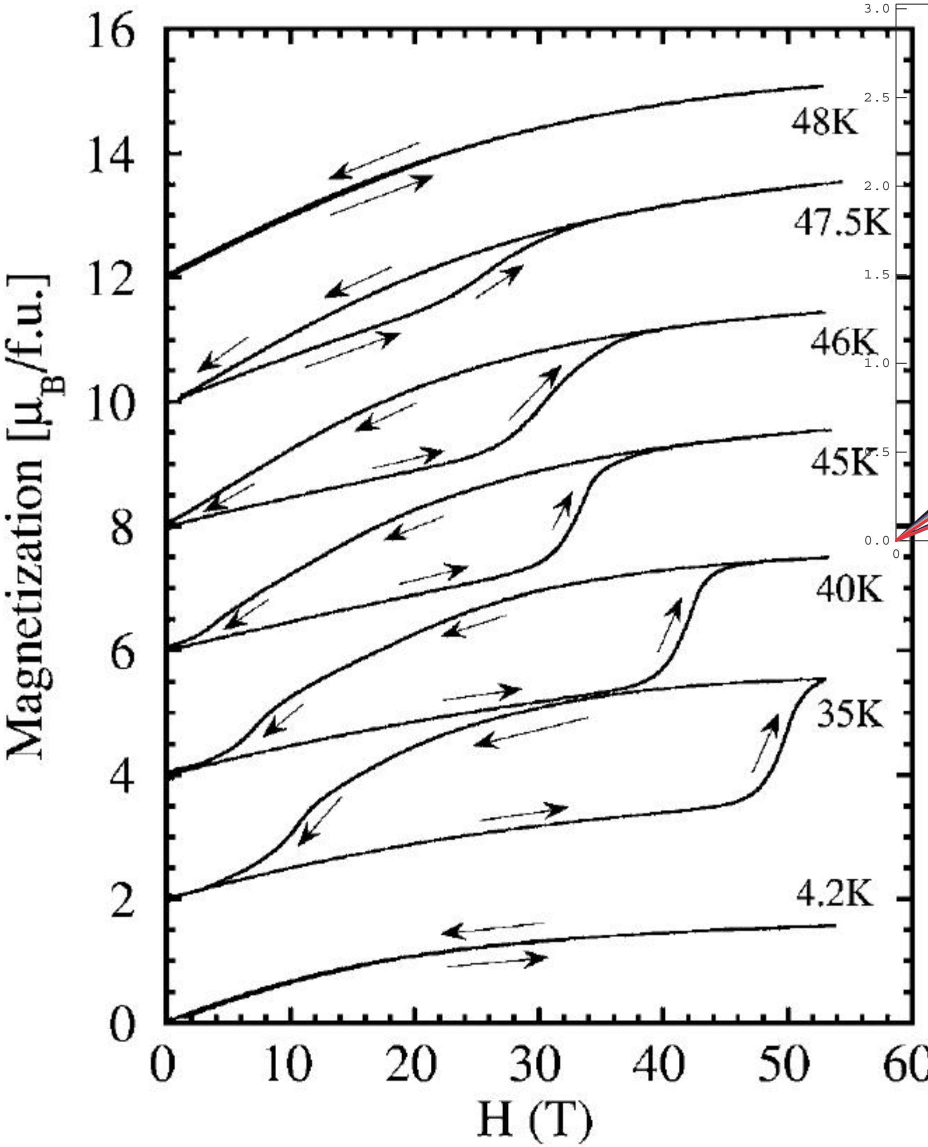
Field-induced SCO in [Mn^{III}(taa)]

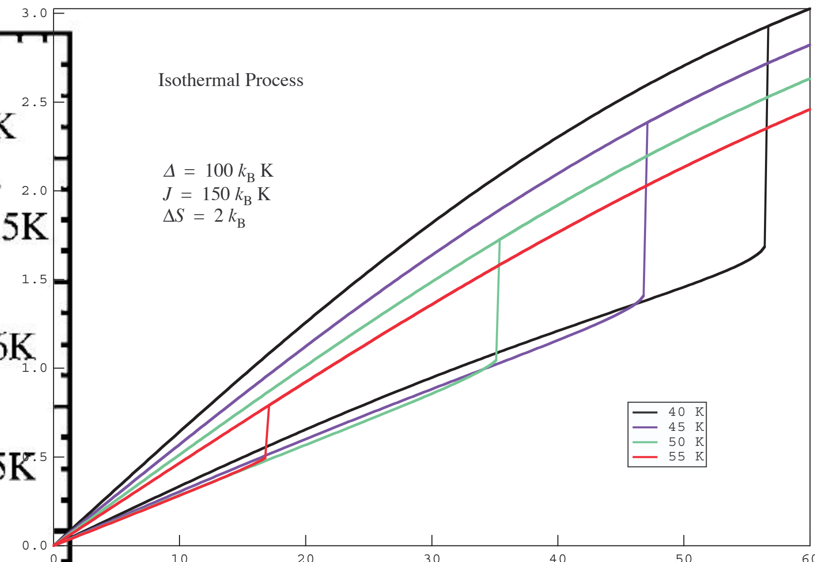




pulse magnet @ Osaka-u

Field-induced SCO in [Mn^{III}(taa)]





parameters in simulation

g_{LS} = 1.6

D_{LS} / k_B = 50.4 K

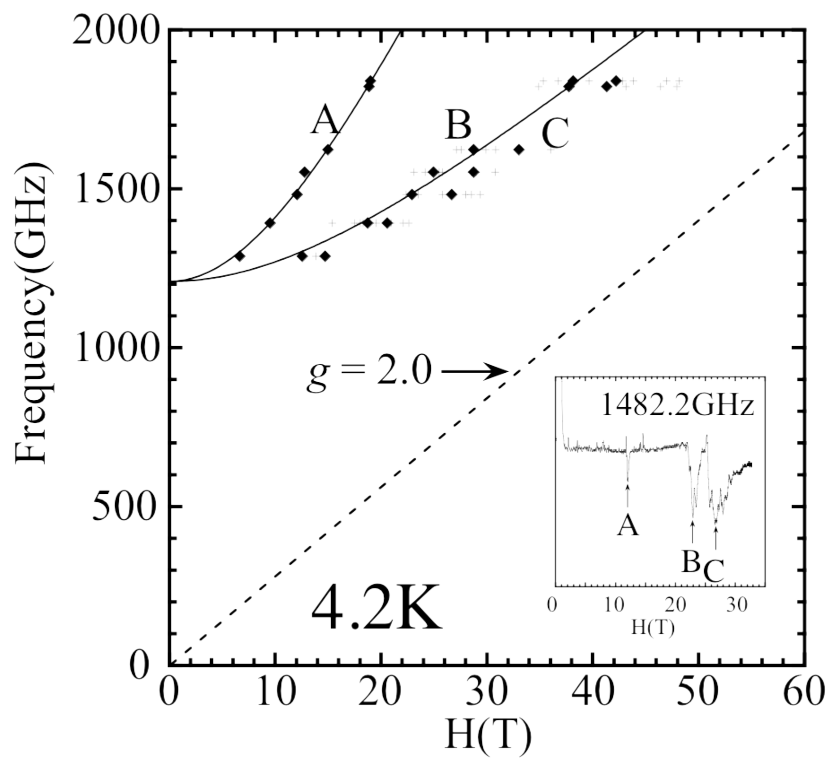
g_{HS} = 2.0

D_{HS} / k_B = –8.49 K

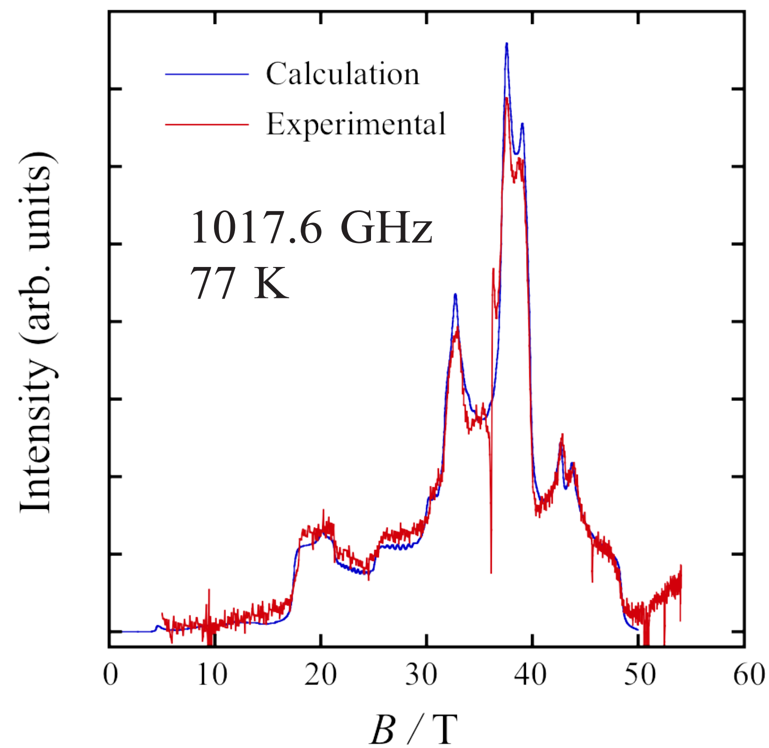
E_{HS} / k_B = 0.72 K

HFEPR of LS and HS states of $[Mn^{III}(taa)]$

LS (S = 1)

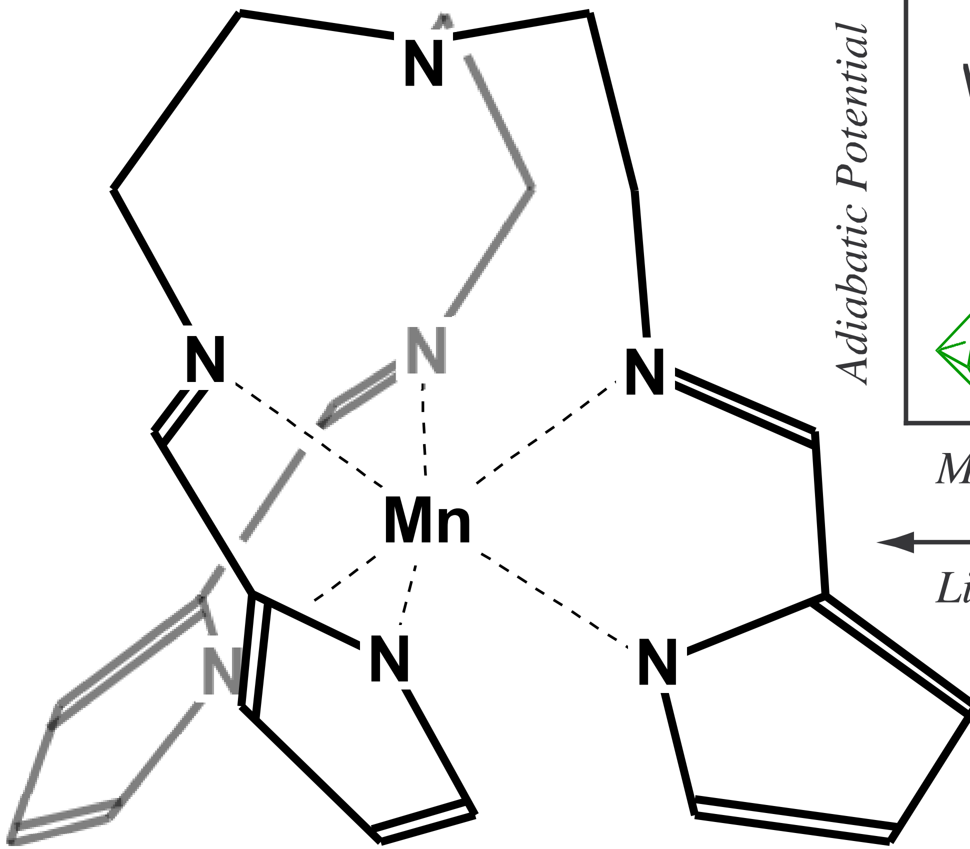


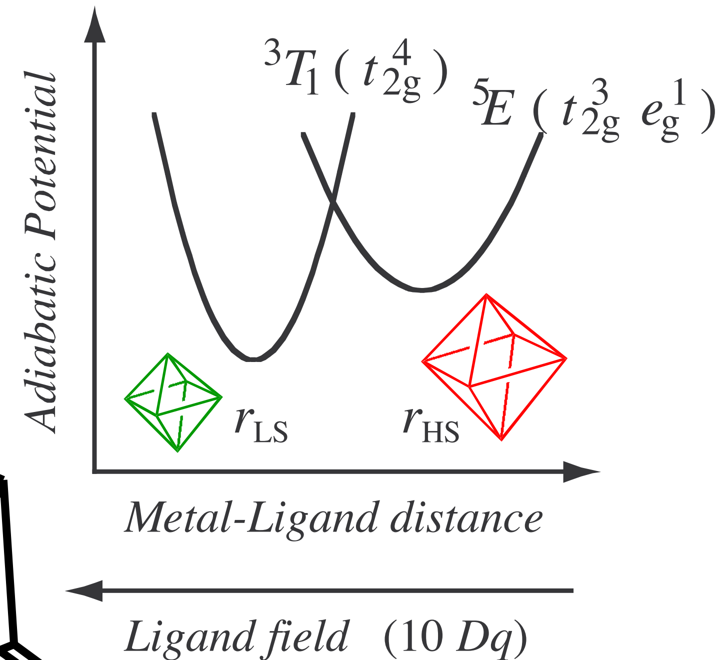
HS (S = 2)



$$\hat{H} = D\left(\hat{S}_z^2 - \frac{1}{3}\hat{S}^2\right) + E\left(\hat{S}_x^2 - \hat{S}_y^2\right) + g\mu_B\mu_0 H \bullet \hat{S}$$

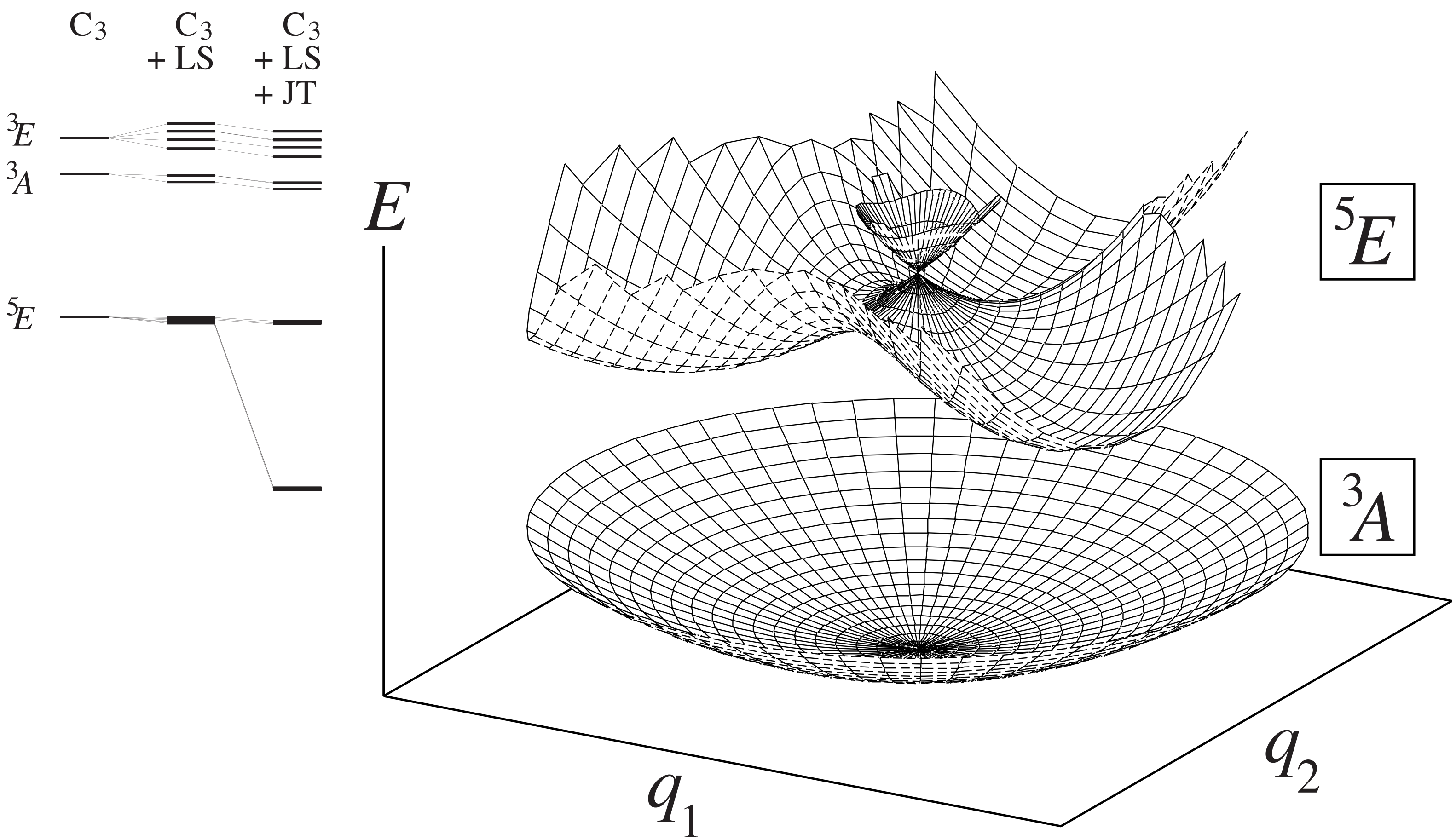
Mn^{III} SCO complex [Mn(taa)]





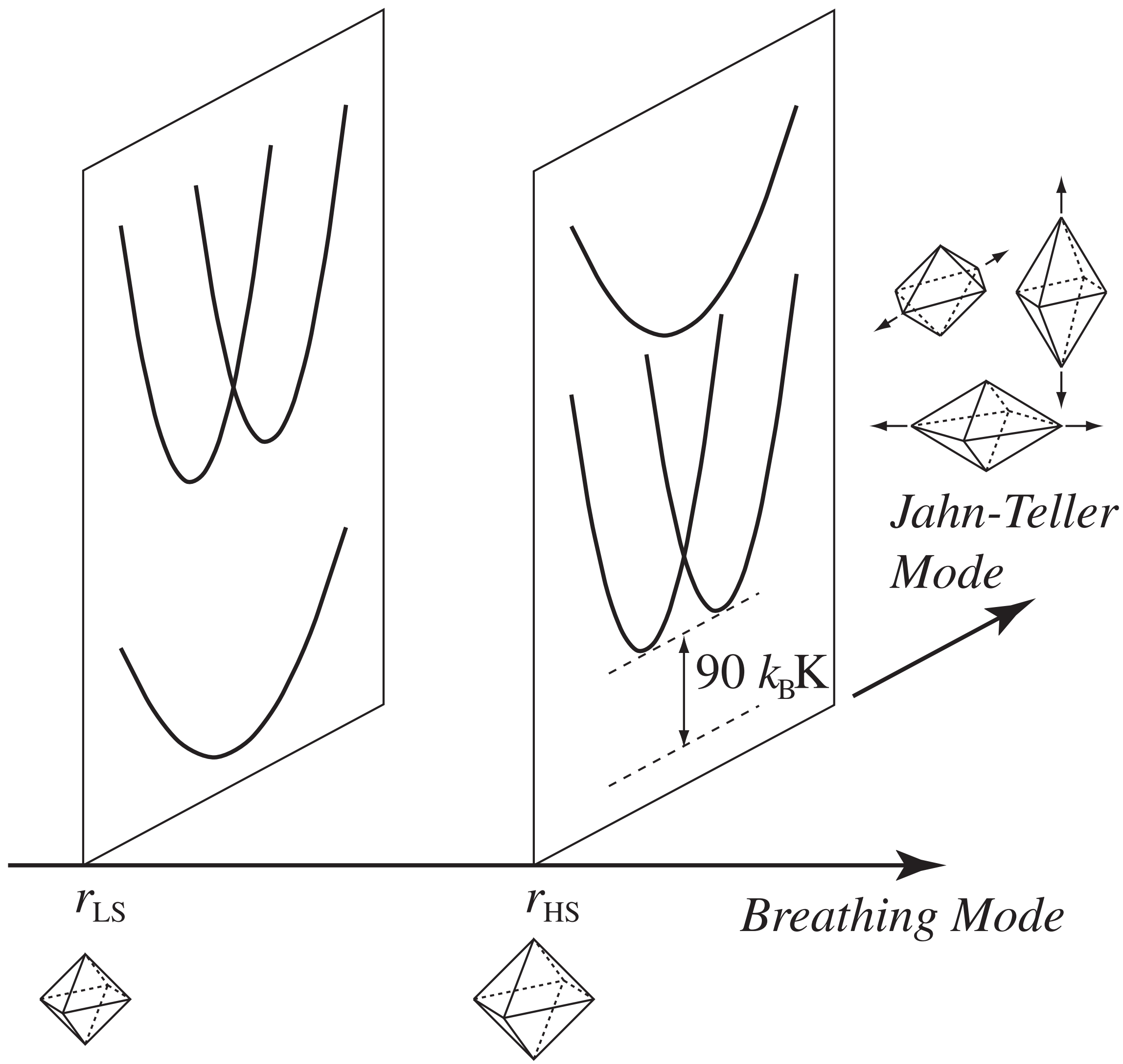
H$_3$taa = tris(1-(2- azolyl)-2-azabuten-4-yl)amine

Electronic states of $[Mn^{III}(taa)]$

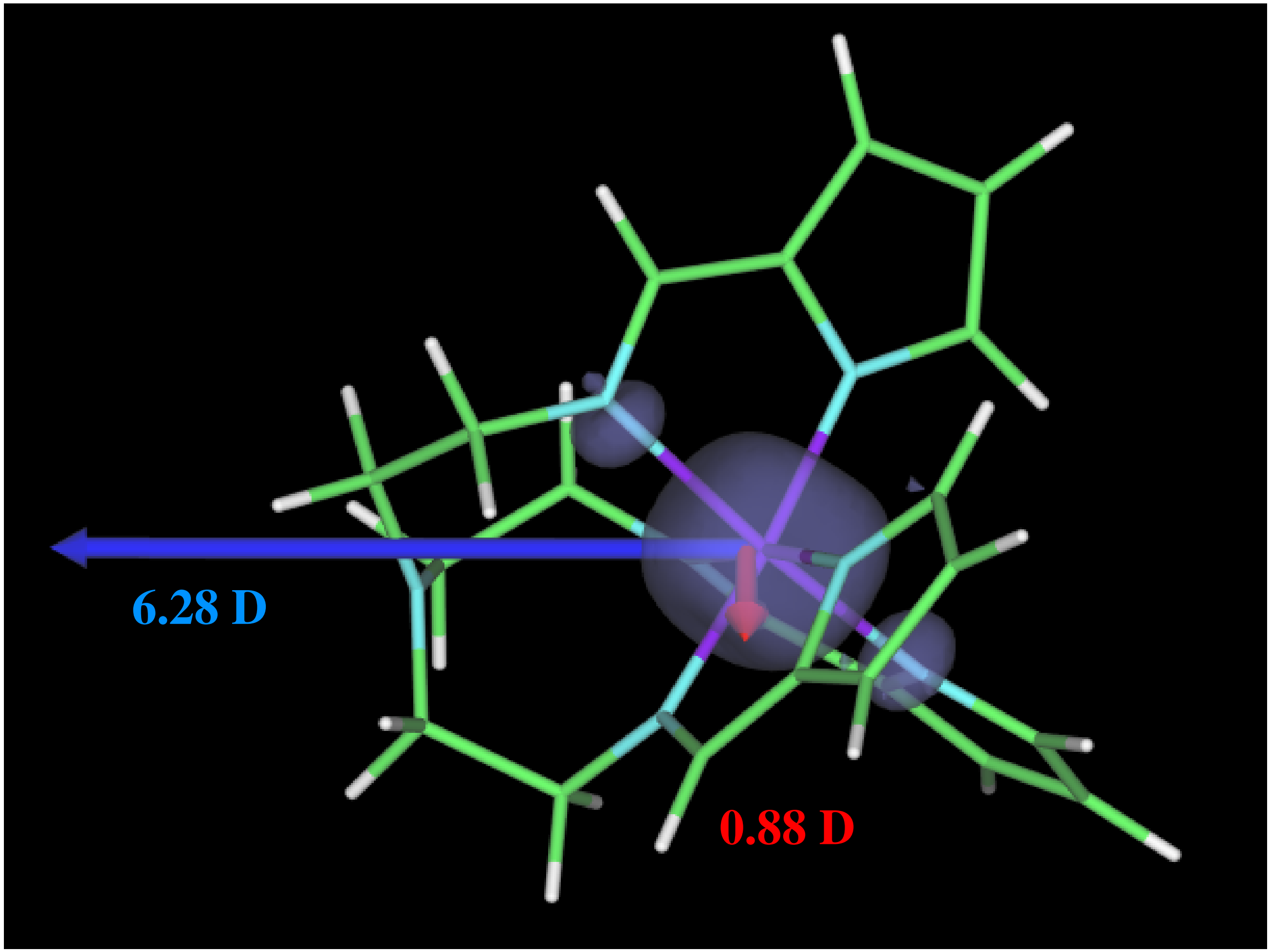


Jahn-Teller instability of HS ^5E state

Active vibrational modes

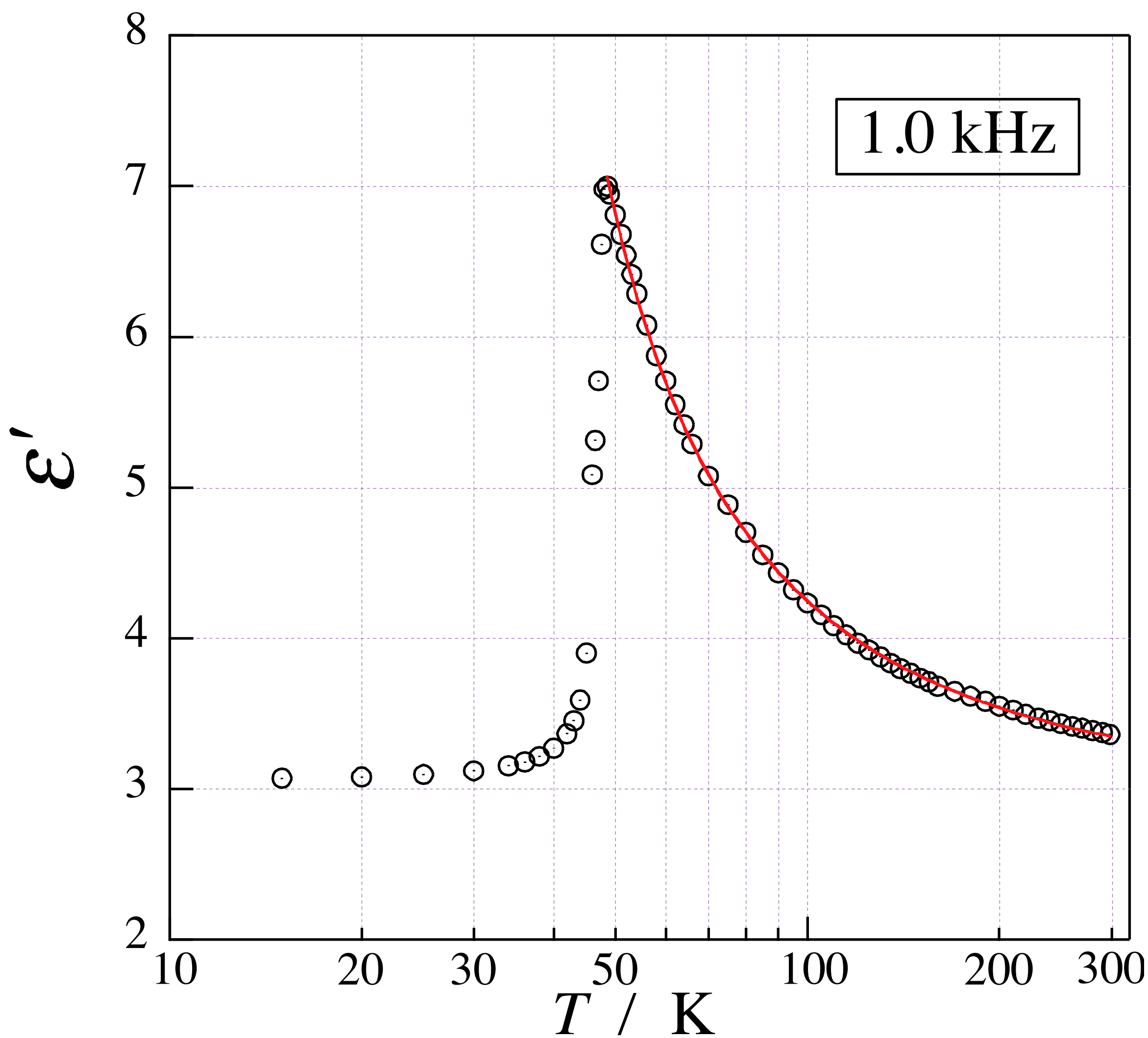


Jahn-Teller distortion in HS species



DFT-optimized structure and spin density isosurface with 0.005 *e* / a.u.^{3}

Dielectric behavior of [Mn^{III}(taa)]



Electrostatics of $[Mn^{III}(taa)]$

Curie behavior of bare dipole: $\boldsymbol{p} = (\mu^2 / 3k_B T)\, \boldsymbol{E}_{loc}$

μ molecular dipole

$\boldsymbol{E}_{loc}$ local field

Macroscopic polarization of crystal: $\boldsymbol{P} = N\, \boldsymbol{p}$

N number density of dipole

Local field $\boldsymbol{E}_{loc} = \boldsymbol{E}_{ext} + \boldsymbol{E}_{Lorentz}$

$= \boldsymbol{E}_{ext} + \boldsymbol{P} / (3\varepsilon_\infty \varepsilon_0)$

ε_∞ high-frequency component

Definition of crystalline dielectric constant ε:

$\boldsymbol{P} = (\varepsilon - \varepsilon_\infty)\, \varepsilon_0\, \boldsymbol{E}_{ext}$

Electrostatics of $[Mn^{III}(taa)]$

Curie-Weiss law: $\varepsilon = \varepsilon_\infty + \dfrac{C}{T - \theta_{es}}$

$C = N\mu^2 / (3k_B\varepsilon_0)$

$\theta_{es} = C / (3\varepsilon_\infty)$ (electrostatic interaction)

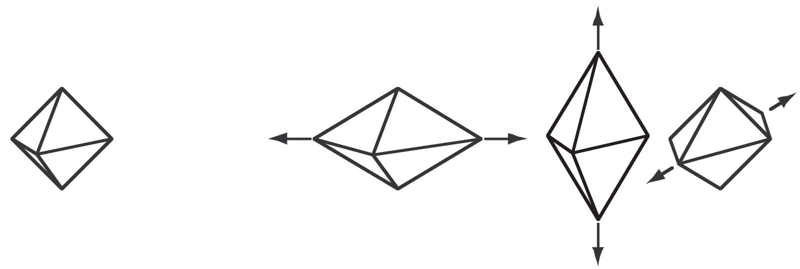
Experimental data $\varepsilon_\infty = 3, C = 91$ K, $\theta = 26$ K

→ estimated molecular dipole $\mu = 1.25$ D

→ van der Waals' interaction $\theta - \theta_{es} = 16$ K

4-State Ising-Potts Model

(Stratt & Adachi, 1987)



ρ_0 ρ_1 ρ_2 ρ_3

LS species ($S_{LS} = 1$) HS species ($S_{HS} = 2$)

Normalization of population

$\rho_0 + \rho_1 + \rho_2 + \rho_3 = 1$

Δ LS-HS gap

J_0 Potts-type interaction between HS species

J_1 Ising-type interaction between HS and LS species

Internal energy:

$$U = \Delta(1 - \rho_0) + J_0(\rho_1^2 + \rho_2^2 + \rho_3^2) + 2J_1\rho_0(1 - \rho_0)$$

Entropy:

$$S/R = \rho_0 \ln(2S_{LS} + 1) + (1 - \rho_0)\ln(2S_{HS} + 1) - \sum_{i=0}^{3} \rho_i \ln \rho_i$$

4-State Ising-Potts Model

Internal energy:

$$U = \Delta(1 - \rho_0) + J_0(\rho_1{}^2 + \rho_2{}^2 + \rho_3{}^2) + 2J_1\rho_0(1 - \rho_0)$$

Entropy:

$$S/R = \rho_0 \ln(2S_{LS} + 1) + (1 - \rho_0)\ln(2S_{HS} + 1) - \sum_{i=0}^{3} \rho_i \ln \rho_i$$

SCF equations:

$$\partial F/\partial\rho_i = 0, \quad \partial^2 F/\partial\rho_i\partial\rho_j > 0 \quad (i, j = 1, 2, 3)$$

3 Stable solutions:

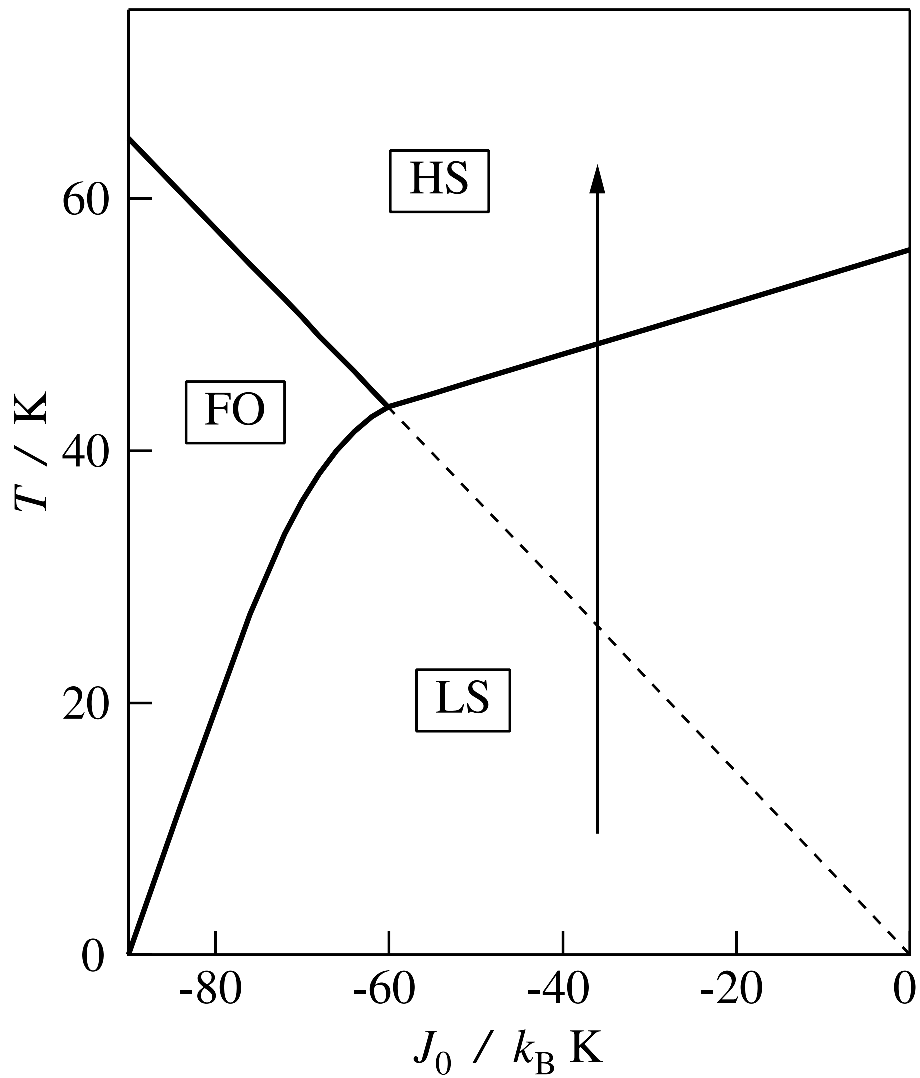
Low-spin (LS) phase $\rightarrow \rho_0 >> \rho_1 = \rho_2 = \rho_3$

High-spin (HS) phase $\rightarrow \rho_0 << \rho_1 = \rho_2 = \rho_3$

Ferrodistortively-ordered (FO) phase

$\rightarrow \rho_0 << \rho_1 = \rho_2 < \rho_3$

Extended Phase Diagram of $[Mn^{III}(taa)]$



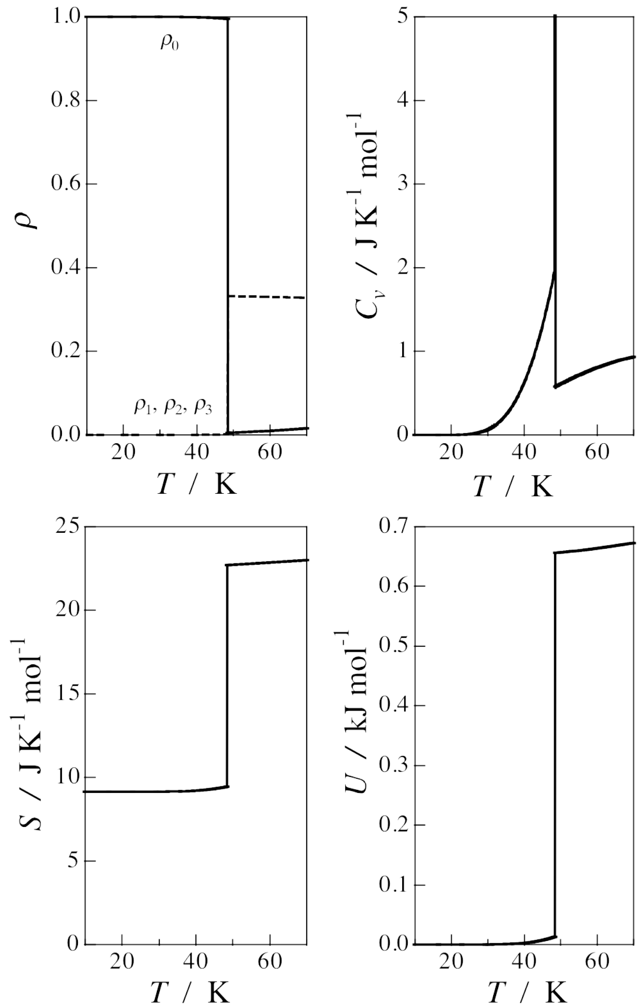
Δ / k_B = 90 K

J_0 / k_B = - 36 K

J_1 / k_B = 125 K

(Δ_{eff} = $\Delta + 2J_1$ = 340 k_B K)

Extended Phase Diagram of [Mn^{III}(taa)]



$\Delta \ / \ k_B \ = \ 90 \text{ K}$

$J_0 \ / \ k_B \ = - 36 \text{ K}$

$J_1 \ / \ k_B \ = 125 \text{ K}$

$(\Delta_{\text{eff}} = \Delta + 2J_1 = 340 \ k_B \text{ K})$

Entropy counting with JT pseudo-rotation

$\Delta S_{mag} = R \ln (2S_{HS} + 1)/(2S_{HS} + 1) = R \ln(5/3)$
$\Delta S_{JT} = R \ln 3$

$\rightarrow \Delta S_{total} = \Delta S_{mag} + \Delta S_{JT} = R \ln 5$
$= 13.4 \text{ J K}^{-1} \text{ mol}^{-1}$

Cf. 13.8 J K^{-1} mol^{-1} based on DSC (Y. Garcia, 2000)

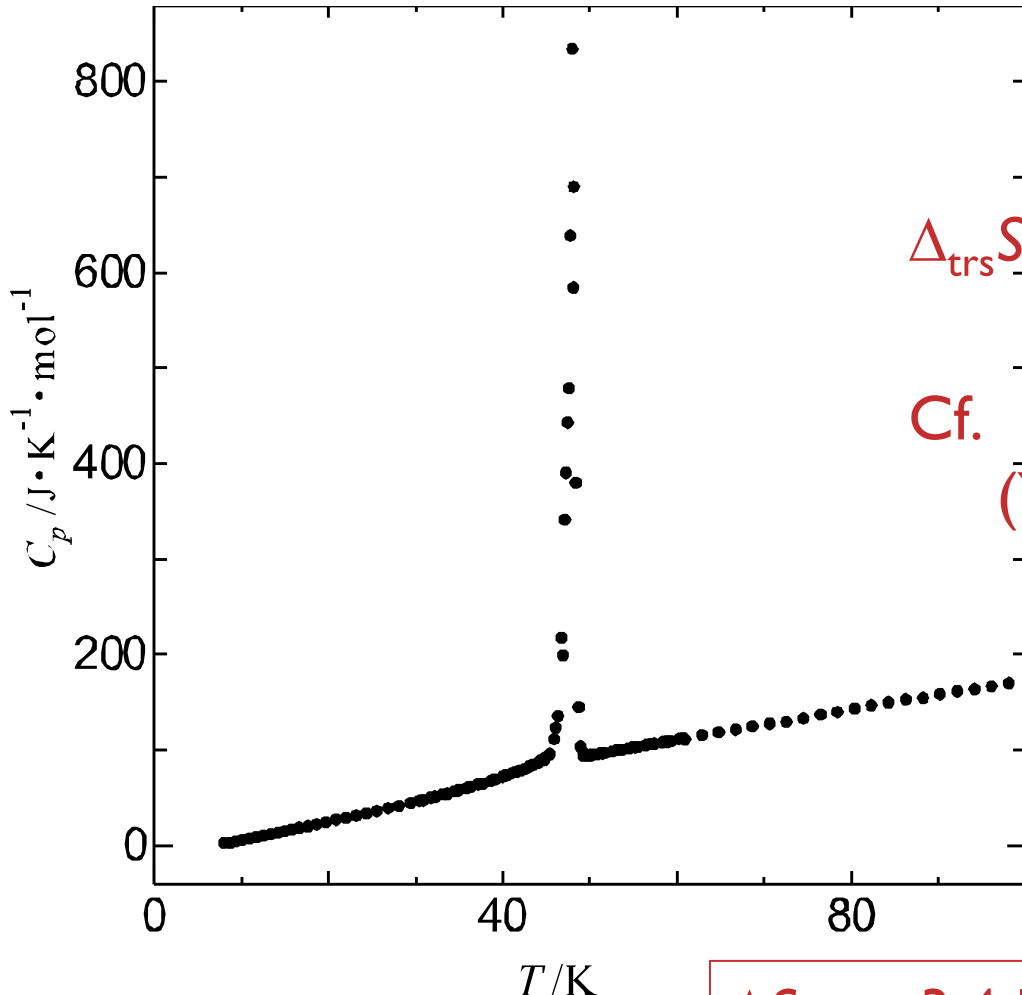
Estimate of the vibrational contribution to the entropy change associated with the spin transition in the d^4 systems [Mn^{III}(pyrol)$_3$tren] and [Cr^{II}(depe)$_2I_2$]†

Yann Garcia,*[a] Hauke Paulsen,[b] Volker Schünemann,[c] Alfred X. Trautwein[b] and Juliusz A. Wolny[bc]

Phys. Chem. Chem. Phys., 2007, **9**, 1194–1201

New estimate $\Delta S_{vib} = 9.1 \text{ J K}^{-1} \text{ mol}^{-1}$

Adiabatic calorimetry of [Mn^{III}(taa)]



$\Delta_{trs}S$ = 16.8 J K^{-1} mol^{-1}

Cf. 13.8 J K^{-1} mol^{-1}
(Y. Garcia, 2000)

ΔS_{vib} ~ 3.4 J K^{-1} mol^{-1}

Perturbation to 4-State Ising-Potts Model

- Pressure effect on χ

  Clamp cell (Cu-Ti alloy)

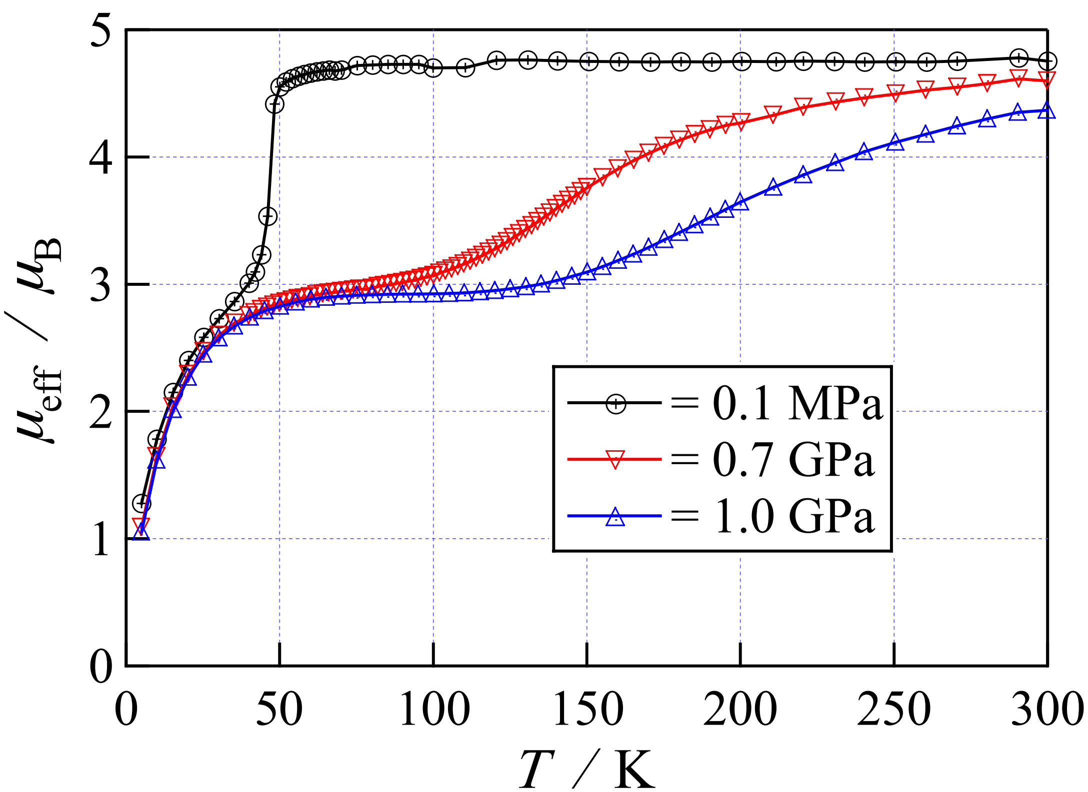
  0.1 MPa to 1.0 GPa

  Fomblin oil – hydrostatic pressure

- Dilution effect on χ and ε

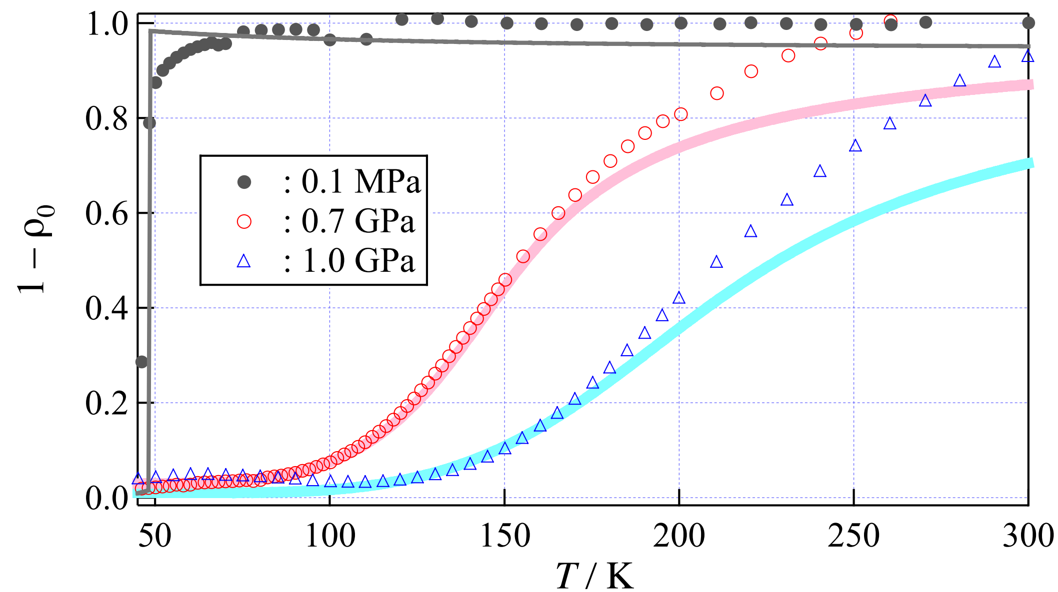
  Mixed crystal [$Mn_{1-x}Ga_x$(taa)]

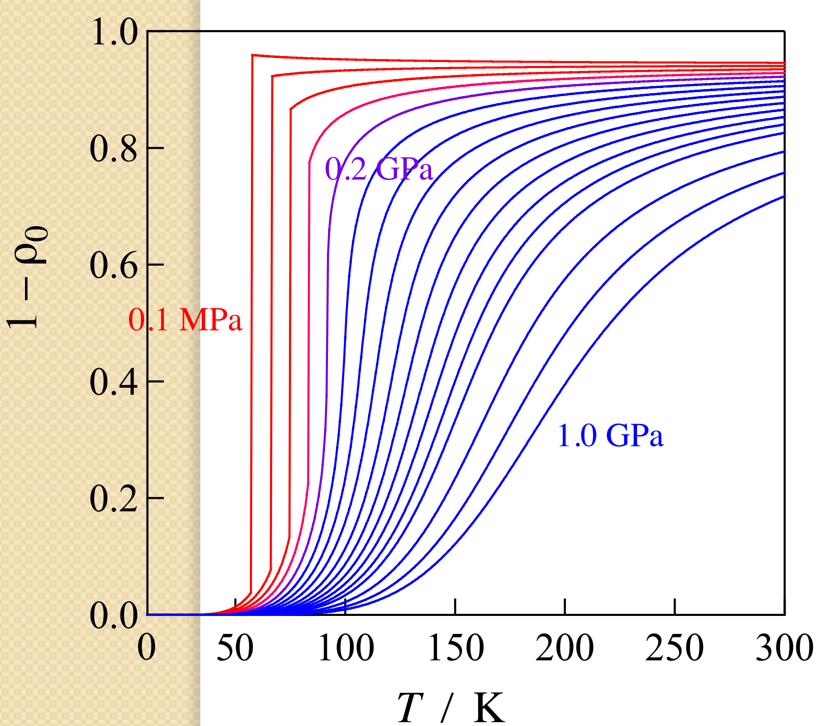
Disappeared transition under pressure



Isomorphic phase transition → critical phenomana?

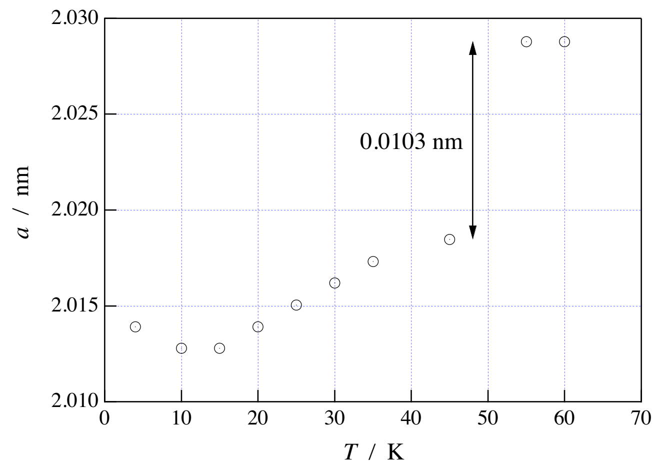
Disappeared transition under pressure

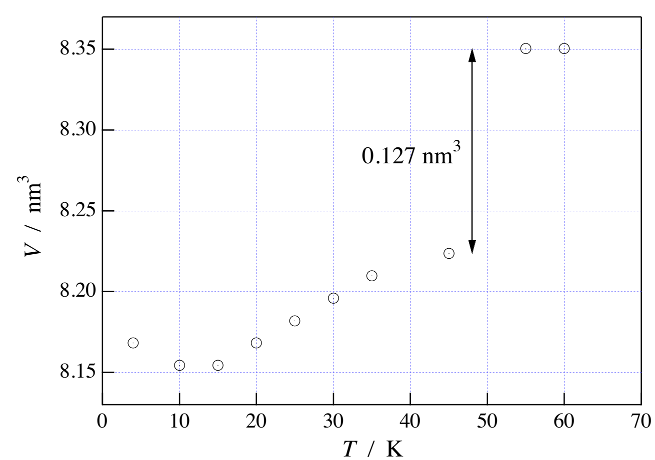




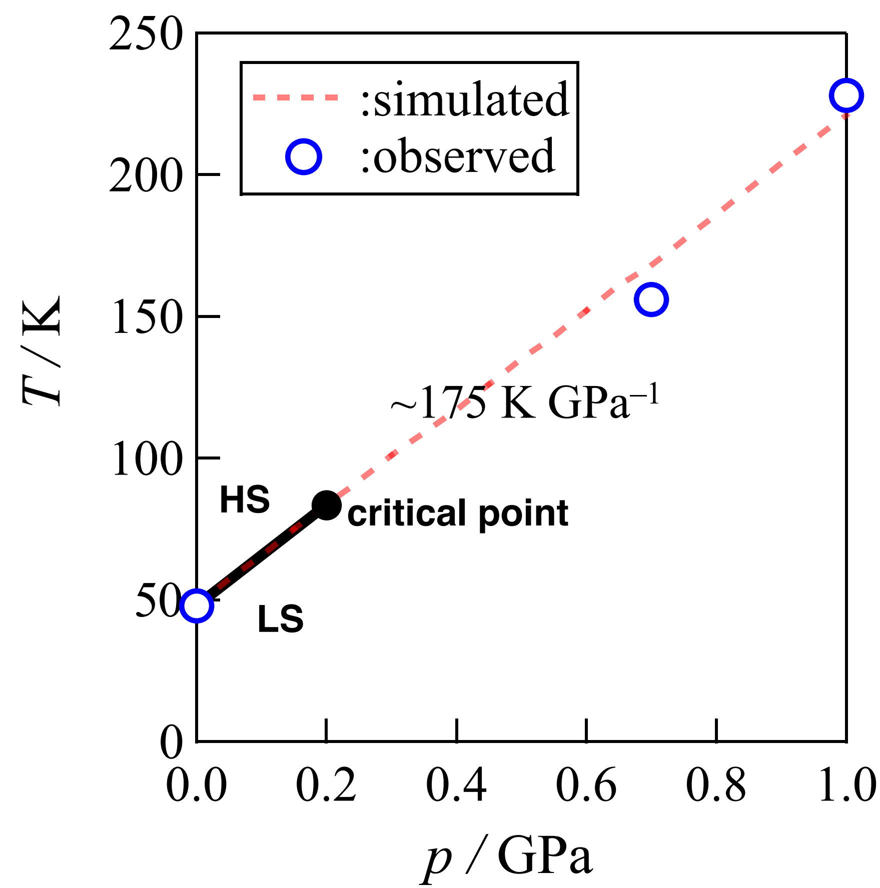
p	Δ / R K	J_0 / R K	J_1 / R K	ΔS_{vib} / R
0.1 MPa	148	-36	96	1.2
0.7 GPa	460	-36	70	1.2
1.0 GPa	660	-36	60	1.2

Disappeared transition under pressure

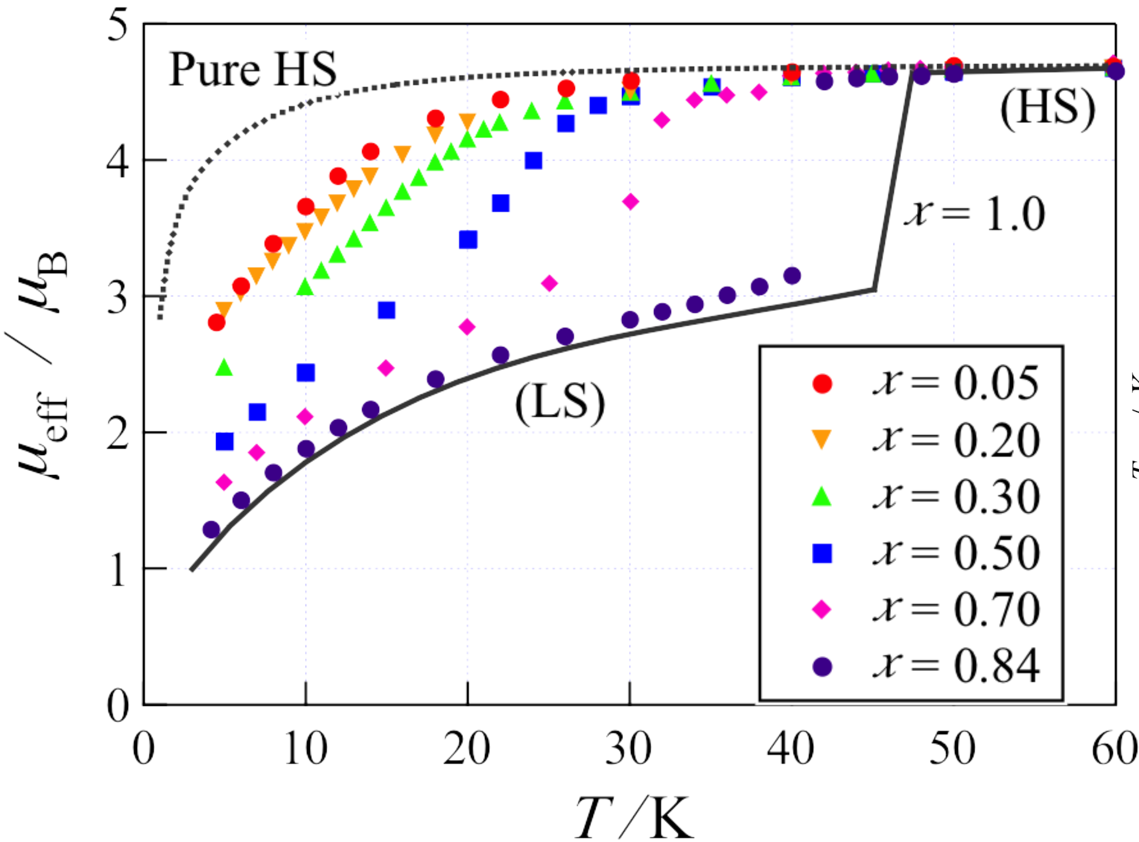


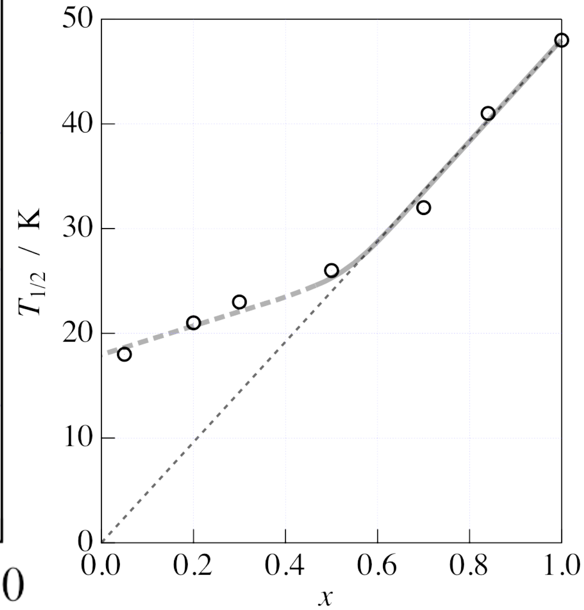


$$\Delta_{trs}V = 4.77\ \mathrm{cm^3\ mol^{-1}}$$



Dilution effect in $[Mn_{1-x}Ga_x(taa)]$



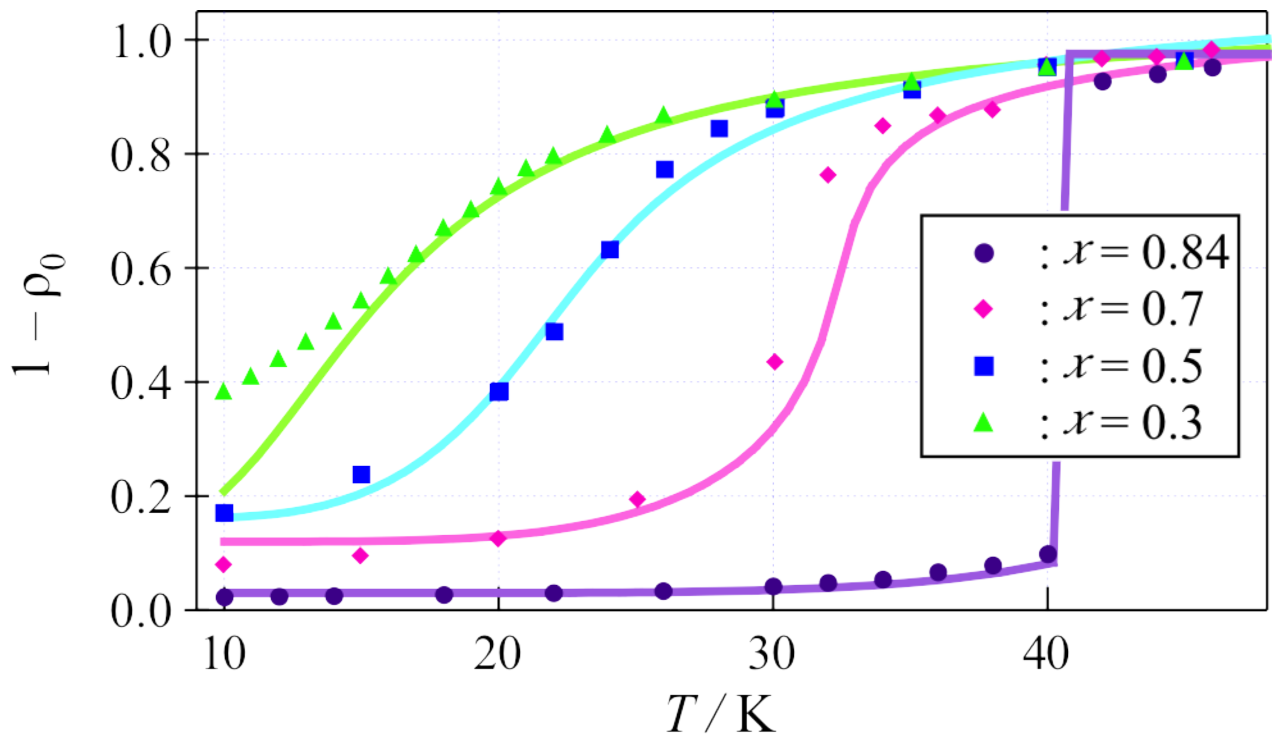


Site-random percolation threshold

simple cubic (z = 6) 0.31

diamond (z = 4) 0.43

Dilution effect in [$Mn_{1-x}Ga_x$(taa)]



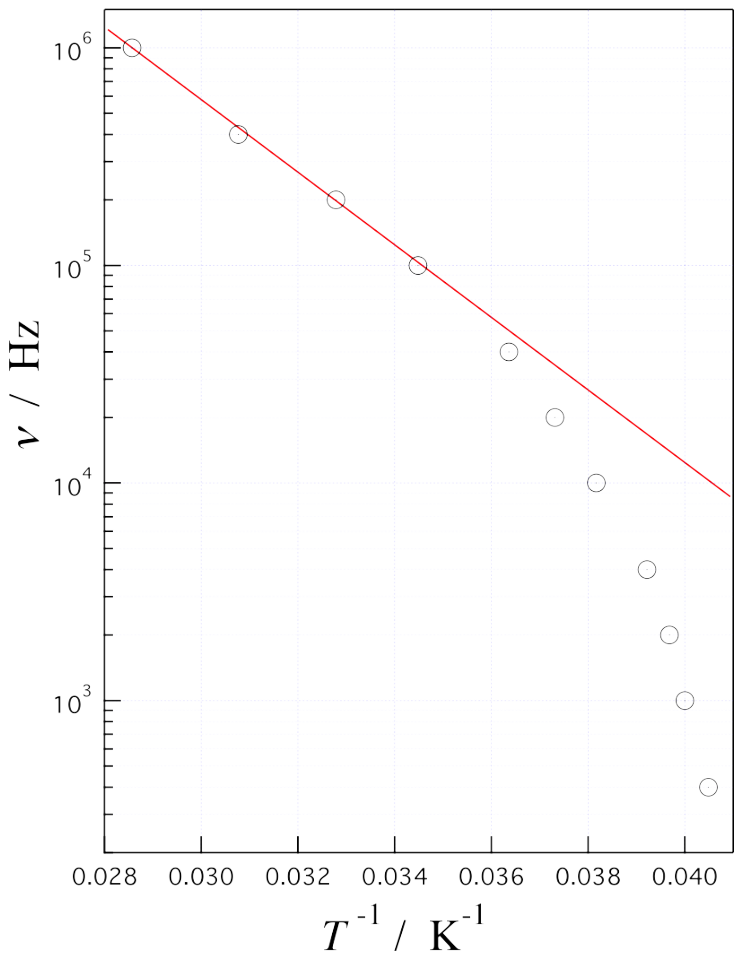
x	Δ / R K	J_0 / R K	J_1 / R K	J_2 / R K	ΔS_{vib} / R
1.00	148	-36	96	–	1.2
0.84	150	-36	80	80	1.2
0.70	150	-36	35	80	1.2
0.50	150	-36	15	75	1.2
0.30	150	-36	0	70	1.2

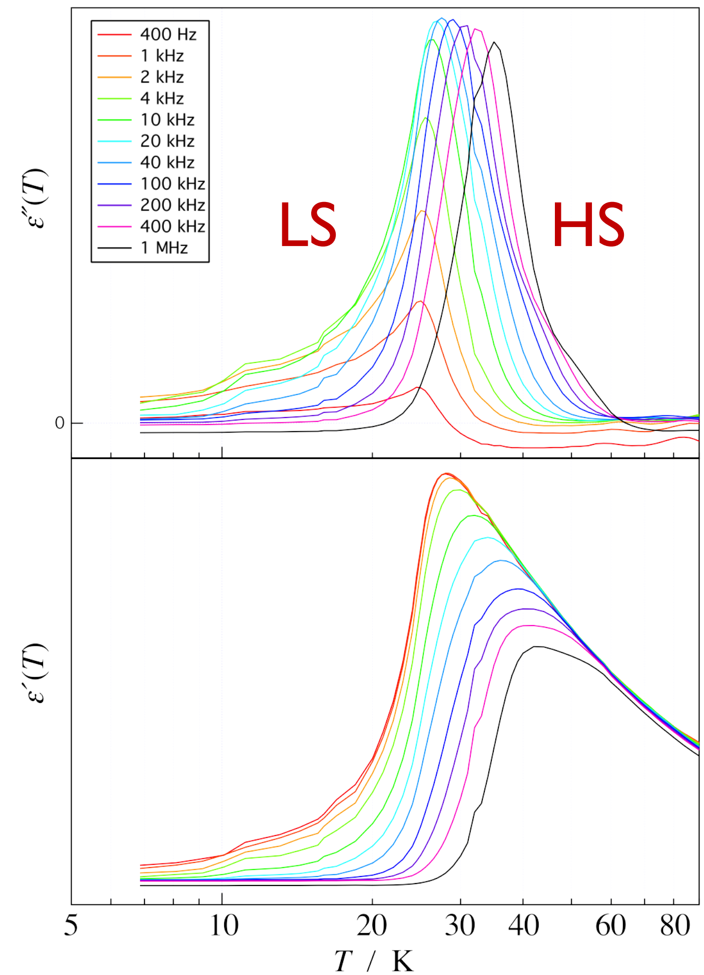
y (= 1 − x)

$$U = \Delta(1-\rho_0-y) + J_0(\rho_1^2+\rho_2^2+\rho_3^2) + 2J_1\rho_0(1-\rho_0-y) + 2J_2\rho_0 y$$

$$S = \rho_0 S_{LS} + (1-\rho_0-y)S_{HS} - R\sum_{i=0}^{3}\rho_i \ln\rho_i$$

Dispersion of ε due to pseudo-rotation





$[Mn_{0.5}Ga_{0.5}(taa)]$

pre-exponential: 0.11 THz

activation energy: 3.4 kJ mol^{-1}

Conclusion

- $[Mn^{III}(taa)]$ is a fascinating system involving two molecular bistabilities and a hidden ferrodistortive order (FO) phase.
- LIESST at low temperature may provide the hidden FO phase. Challenging!

Acknowledgements

Dielectric measurement

Prof. T. Matsuo (Osaka Univ.)
Prof. O. Yamamuro (ISSP, Univ. Tokyo)

High magnetic field

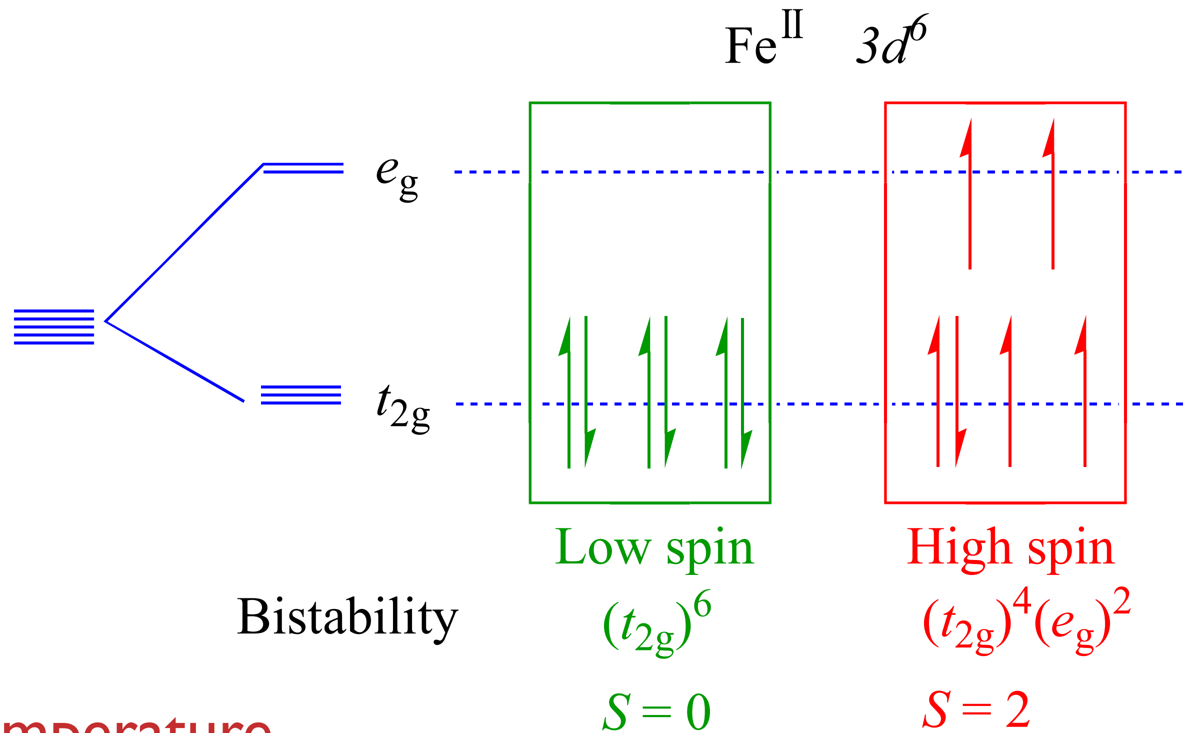
Prof. Y. H. Matsuda (ISSP, Univ. Tokyo)
Prof. S. Kimura (Tohoku Univ.)
Prof. Y. Narumi (Osaka Univ.)

High pressure

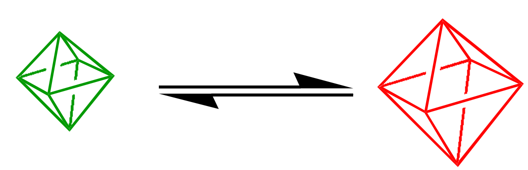
Prof. Y. Hosokoshi (Osaka Pref. Univ.)

Spin-crossover (SCO) phenomena

Octahedral transition metal complex

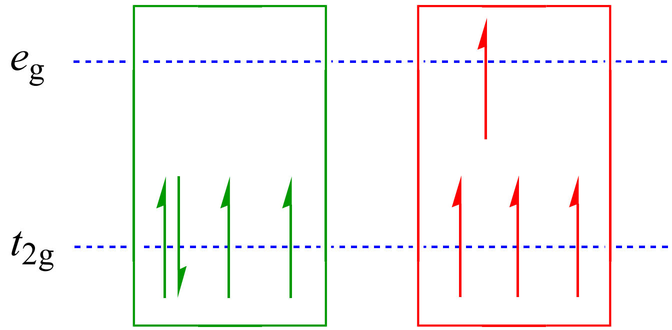


Temperature
Pressure
Magnetic field
Light irradiation …

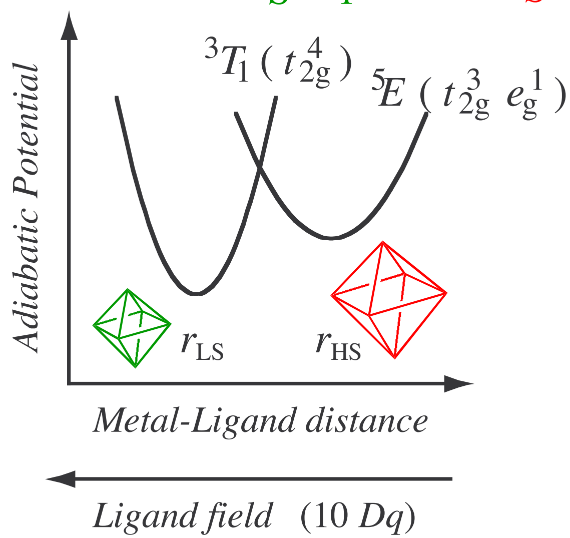


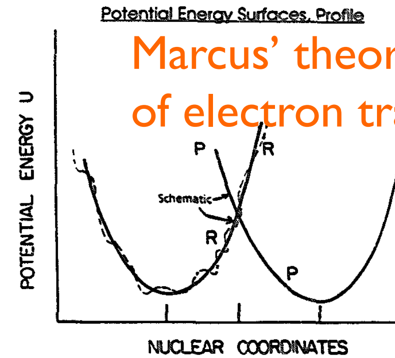
Vibrational degree of freedom in SC

Mn^{III}
(3d)^4

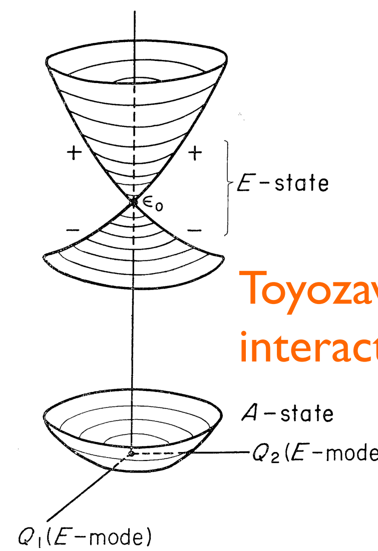


Low spin	High spin
$(t_{2g})^4$	$(t_{2g})^3(e_g)^1$
$S = 1$	$S = 2$





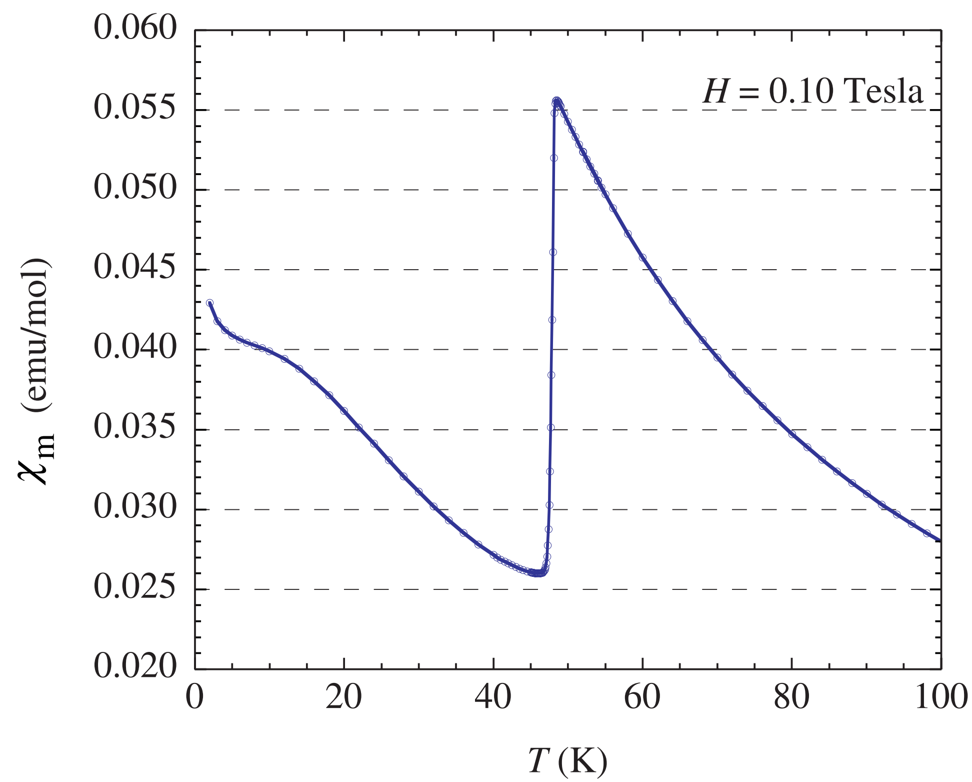
Marcus' theory
of electron transfer (1956)

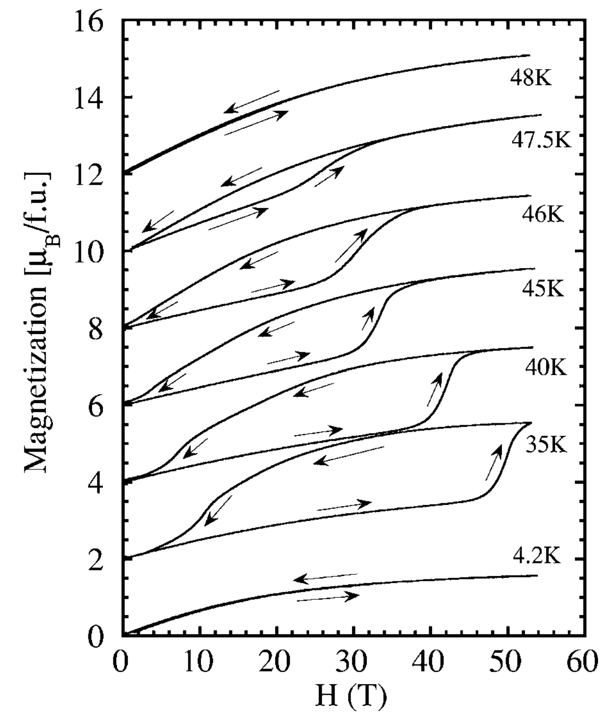


Toyozawa's
interaction mode (1966)

SCO : single-center electron transfer

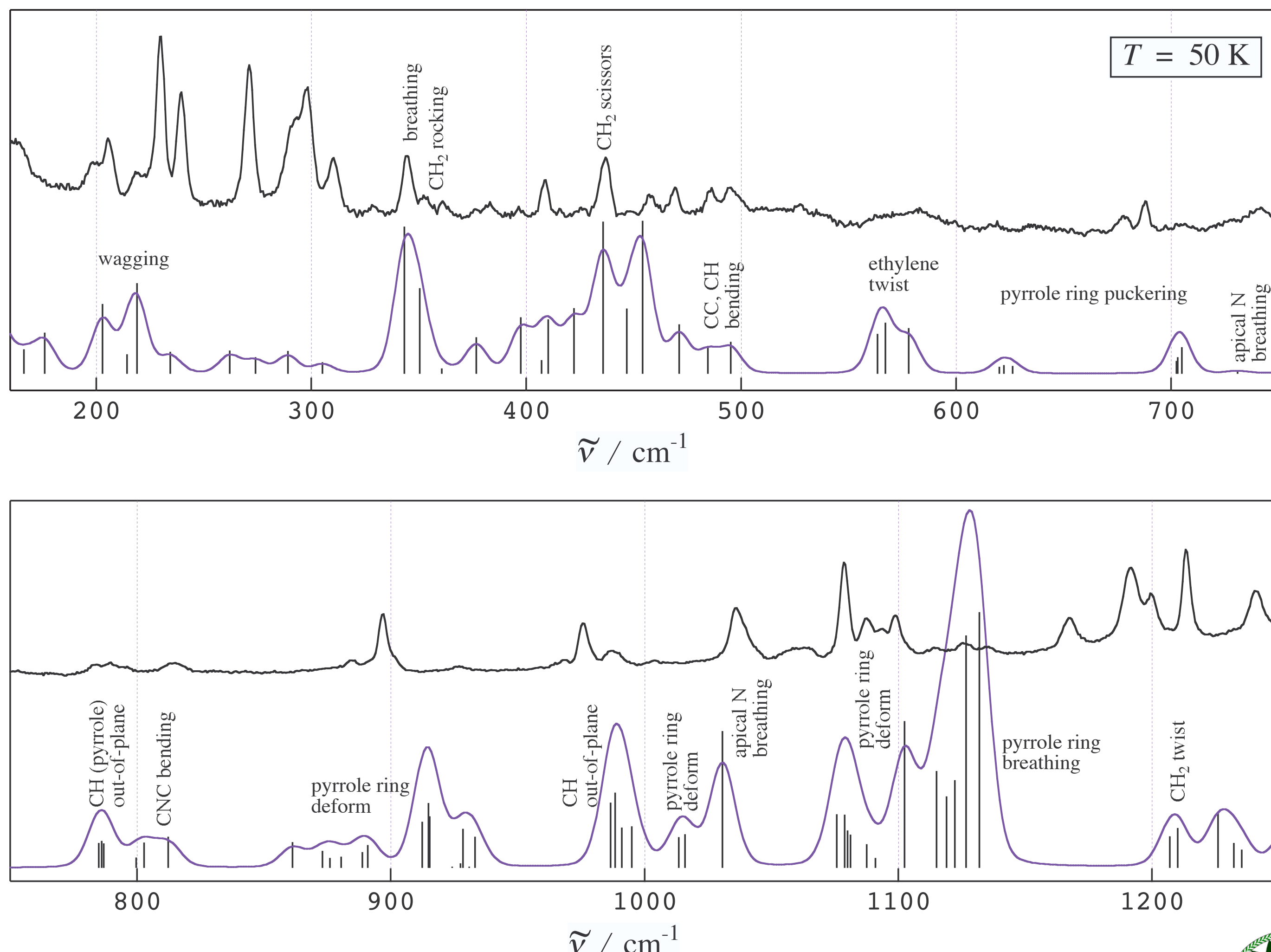
Mn^{III} SCO complex [Mn(taa)]





T_C= 48 K

Raman spectra of [Mn^{III}(taa)]



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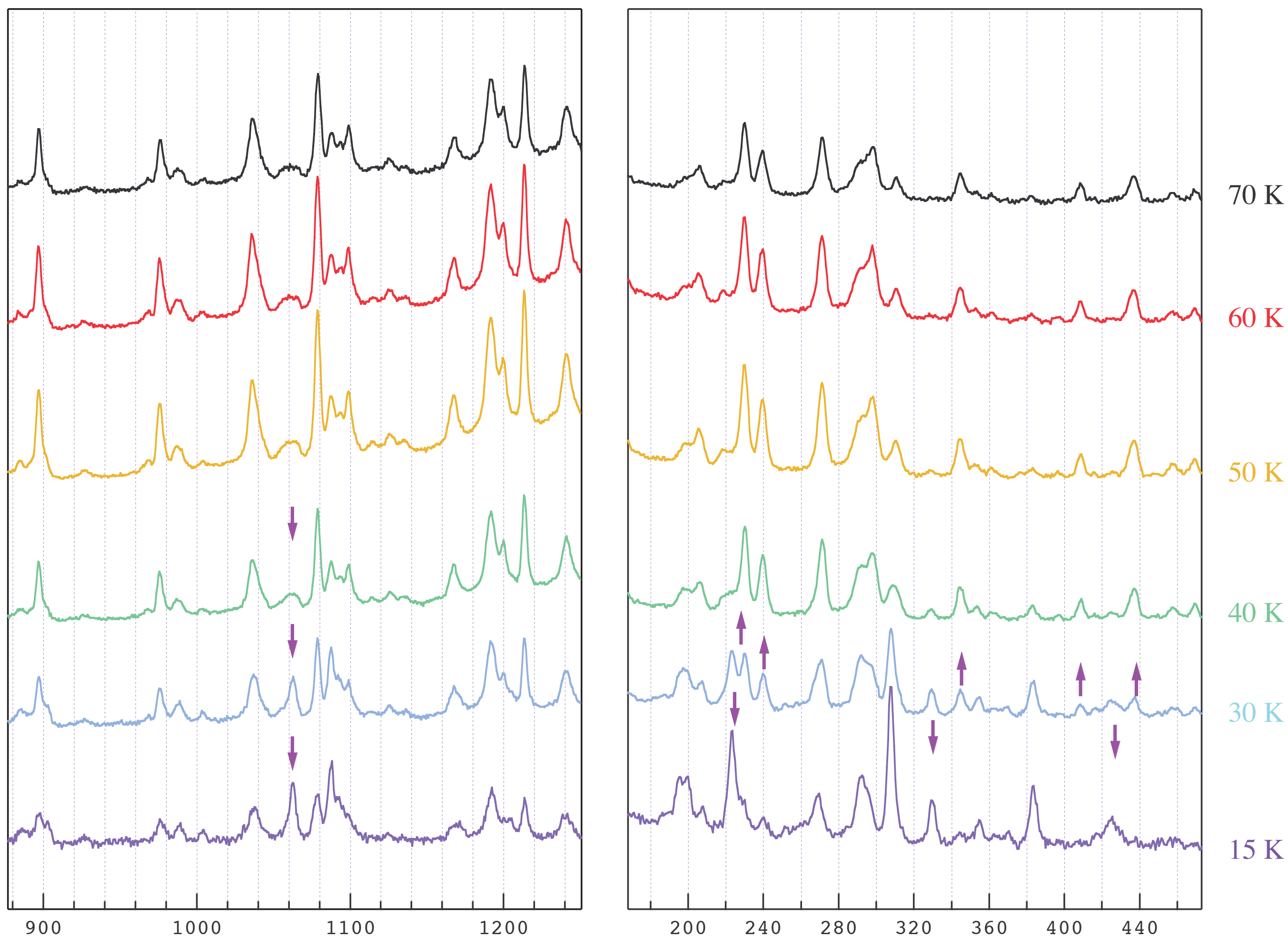
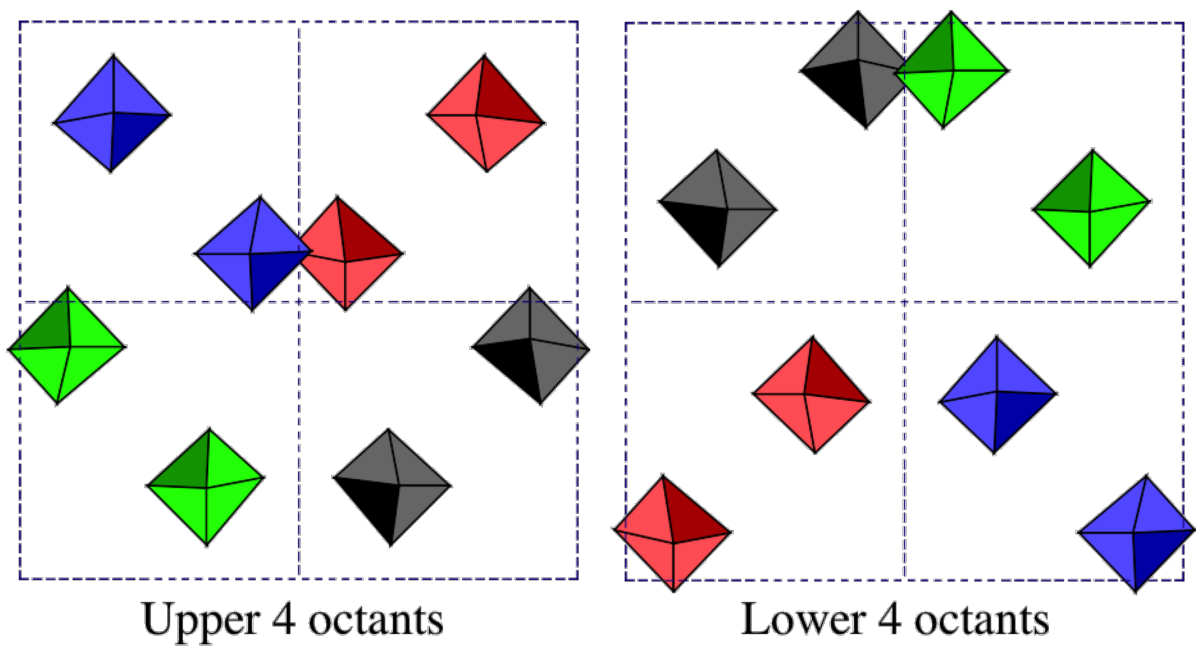


Crystal structure of $[Mn^{III}(taa)]$

HS phase
space group *I-43d* (cubic)
Z = 16
a = 2.0309 nm



H-T phase diagram of [Mn^{III}(taa)]