Mean Field Modeling of FeII Spin Crossover Systems in a Magnetic Field[#]

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Abstract

The modeling of Spin Crossover systems with a special focus on molecular vibrations and on the effect of a magnetic field is developed and discussed. Two different theoretical models are applied, namely: a thermodynamic model and an Ising like model including molecular vibrations. A combination two already existing Ising like models – one including the effect of an external magnetic field and the other taking molecular vibrations into account - is outlined and discussed. In all calculations a field dependency of the Spin Crossover transition temperature $T_{1/2}$ is evident. An external magnetic field induces a downward shift of $T_{1/2}$. This corresponds to results of high magnetic field experiments and thermal expansion measurements [1, 2].

Introduction

In a series of transition metal complexes a change of the spin state of the central ion can be initiated by external perturbations such as temperature, light, pressure or magnetic field. Besides the well known change of color and magnetic properties [3-5], the spin transition is accompanied by an important change of the dielectric constant within a wide frequency range (kHz-THz-vis) [6]. Considering these properties, Spin Crossover (SCO) materials seem promising tools for actual technical applications like displays, data-storage [7] and even gas

sensing devices taking into account that the absorption of gas and vapor molecules strongly influences the transition behavior [8]. In fact various nanostructures of these compounds have already been formed [9, 10].

The application of a magnetic field on spin crossover compounds stabilizes the HS state, which yields to a field induced downward shift of the thermal Spin Crossover [1, 11, 12]. At first, Sasaki and Kambara predicted this effect for high fields with a model based on the cooperative Jahn Teller effect [13]. Based on these suggestions several models have been proposed which are discussed in [14]. The present work focuses on modeling the influence of an external static magnetic field on the spin transition by means of two different approaches: one based on the framework of the Gibbs free energy as presented in [11, 12, 15], and the other one is based on an Ising like model combining previously presented models including molecular vibrations [16-18] with the models taking the effect of an external magnetic field into account [19-21].

1. Thermodynamic approach within the framework of the Gibbs free energy

The phenomenological Ising like Hamiltonian is appropriate for the description of both, the high-spin state (HS) and the low-spin state (LS) of a given SCO system.

$$\hat{H}^z = \frac{\Delta_0}{2} \sum_i \hat{\sigma}_i - J \sum_{i \neq j} \hat{\sigma}_i \hat{\sigma}_j \tag{1}$$

Herein $\hat{\sigma}_i$ is the so called fictitious spin operator with the eigenvalues $\sigma = -1$ for the LS state and $\sigma = +1$ for the HS state. The energies and degeneracies of this 2 level system can be expressed as a function of the energy gap Δ_0 and the phenomenological parameter J, which comprises the intermolecular interactions.

The application of a magnetic field removes the degeneracies of both, the HS and LS levels. As a result the new Hamiltonian can be written as [22, 23]:

$$\hat{H}^z = \frac{\Delta_0}{2} \sum_i \hat{\sigma}_i - J \sum_{i \neq j} \hat{\sigma}_i \hat{\sigma}_j \pm \frac{g \mu_B B_Z \hat{S}_z^{H,L}}{\hbar} \sum_i \hat{\sigma}_i^{H,L} \tag{2}$$

where μ_B is the Bohr Magneton, g the Landé factor, B the magnetic field and S_Z is the projection of the spin moment along the field direction.

Within the mean field approach the spin-spin interaction term becomes [21]:

$$J\sum_{i\neq j}\hat{\sigma}_i\hat{\sigma}_j \rightarrow J\langle\sigma\rangle\hat{\sigma}$$

One can now calculate an implicit expression for the field dependency of the spin transition temperature $T_{1/2}$ within a framework of a thermodynamic model based on Gibbs free energy.

The spin transition temperature $T_{1/2}$ is the temperature at which $x_{HS} = x_{LS} = 0.5$. A thermally induced Spin Crossover can be characterized by $x_{HS} = \dfrac{n_{HS}}{n_{HS} + n_{LS}}$, representing the mole ratio of the HS molecules.

$$\Delta G = G_{HS} - G_{LS} = \Delta H(0) + p\Delta V - T\Delta S(0) - B\Delta M \tag{3}$$

$\Delta H(0)$ and $\Delta S(0)$, enthalpy and entropy difference between LS and HS state, refer to the properties of the system in absence of an external field. $\Delta M = M(x)_{HS} - M(x)_{LS}$ (see equation (4)) stands for the difference of the magnetization between the respective spin states. The product $-B\Delta M$ however represents the magnetic free energy difference between the (LS) state and (HS) state.

The magnetization $M(x)$ (Brillouin function) can be derived from the magnetic contribution [18] to the canonical partition function of the Ising like Hamiltonian (2):

$$M(x) = N_A g\mu_B \left(\coth\left(x(S+\frac{1}{2})\right)\left(S+\frac{1}{2}\right) - \coth\left(\frac{x}{2}\right)\right) \tag{4}$$

where $x = \dfrac{g\mu_B B_Z}{k_B T}$.

This yields to an implicit equation for the field dependency of the transition temperature $T_{1/2}(B)$ in the spin equilibrium, where $\Delta G = 0$:

$$\Delta G = \Delta H(0) - T\Delta S(0) - B\Delta M(T) = 0 \tag{5}$$

With $\dfrac{\Delta H(0)}{\Delta S(0)} = T_{1/2}(0)$ this leads to:

$$T_{1/2}(B) = \frac{T_{1/2}(0)}{1 + \dfrac{B}{\Delta H(0)} \Delta M(T_{1/2}(B))}$$

(6)

Contrary to previous approaches as seen in [19], which are only valid for $g\mu_B \ll k_B T_{1/2}$, and result in an analytic solution for equation (6) that is quadratic in the magnetic field as

$T_{1/2}(B) - T_{1/2}(0) = \delta T_{1/2} = -\dfrac{4(\mu_B B)^2}{k_B \Delta(0)}$, no approximations have been made for equation (4).

Due to its complexity equation (6) was solved numerically.

Fig. 1 presents the calculated downward shift of the transition temperature $\delta T_{1/2} = T_{1/2}(B) - T_{1/2}(0)$ for the complex Hexakis(1-propyltetrazole)iron(II)Bis(tetrafluoroborate) - [Fe(ptz)$_6$(BF$_4$)$_2$] [3]. The difference between these two approaches is increasing for higher magnetic fields.
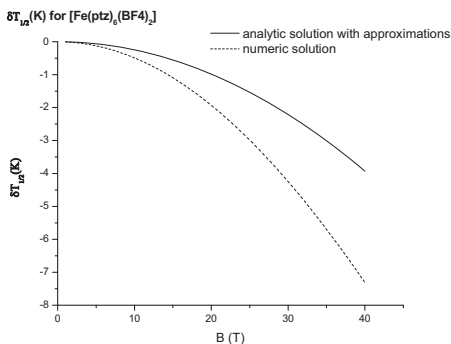

Fig. 1 The 2 curves represent the shift of the transition temperature as a function of the applied field. The solid line represents an approach which is only valid for relatively small fields and high temperatures. However an analytical solution can be calculated [19]. The dashed line represents a numerical calculation of the transition temperature as presented above. The degeneration of the orbitals is completely neglected in both approaches. The values have been gained through caloric measurements on [Fe(ptz)$_6$(BF$_4$)$_2$] [24] $\Delta H = 6108 J$, $T_{1/2} = 135 K$

In fig. 2 one can see the field dependency of the Spin Crossover transition temperatures $T_{1/2}(B)$ as a function of the external magnetic field for the two Spin Crossover compounds Tris(1,4 bis(tetrazole – 1-yl) butane) iron(II)Bis(tetrafluoroborate) - [Fe(4ditz)$_3$(BF$_4$)$_2$] [25] and for [Fe(ptz)$_6$(BF$_4$)$_2$] with the experimentally gained parameters $\Delta H, \Delta S$ and $T_{1/2}(0)$ [2, 26].

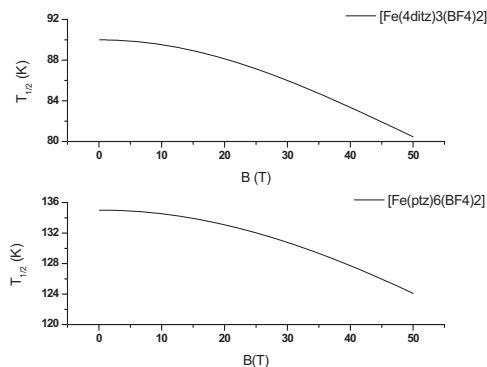**Fig. 2** Shift of transition temperature versus applied magnetic field for $[Fe(ptz)_6(BF_4)_2]$ with the experimentally gained parameters $\Delta H = 6108\,\dfrac{J}{mol}, \Delta S = 50.9\,\dfrac{J}{Kmol}$ and $[Fe(4ditz)_3(BF_4)_2]$ with the parameter set $\Delta H = 6177\,\dfrac{J}{mol}, \Delta S = 68.63\,\dfrac{J}{Kmol}$ The degeneration of the orbitals is completely neglected in this approach.

The compound $[Fe(4ditz)_3(BF_4)_2]$ crystallizes in the space group P1 with one formula unit of the complex per unit cell. Three independent networks interpenetrate each other[27]. Fig. 3 displays the structure of the $[Fe(4ditz)_3(BF_4)_2]$ complex. The compound $[Fe(ptz)_6(BF_4)_2]$ has a rhombohedral spacegroup R3 with a hexagonal lattice structure (Z=3). A detailed survey investigating the structural details of $[Fe(ptz)_6(BF_4)_2]$ can be found in [28].

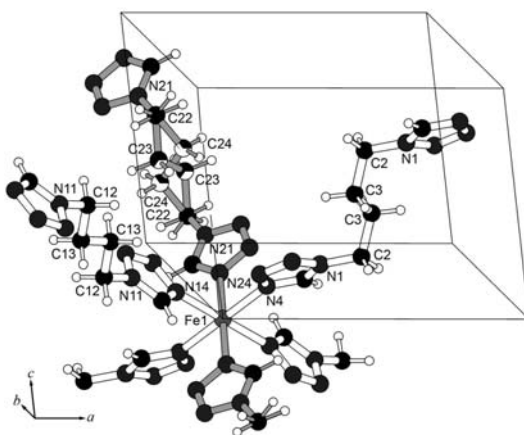**Fig. 3** Coordination environment of Fe^{II} in $[Fe(4ditz)_3(BF_4)_2]$ at 89K. The 4ditz – chain is colored dark grey; the partially occupied carbon atoms (C23 and C24) are marked with sectors. The unit cell is displayed [27].

Recent developments in theoretical modeling [29] show the importance of intermolecular vibrations as a driving force of thermally induced Spin Crossover. This encouraged us to include these vibrations in a more detailed model.

2. Ising like model including molecular vibrations for SCO systems under the influence of an external magnetic field

The consideration of molecular vibrations clearly affects the partition function. Besides the electronic and magnetic contributions it now also contains the vibronic contributions.

The effect of intermolecular vibrations on SCO compounds has been extensively studied by Bousseksou et al. in [16].

Considering each molecule as a set of (3n-6) harmonic oscillators with the "fundamental" vibrational frequencies ν_{HS}^i and ν_{LS}^i. This can be interpreted as possible vibrations of a metal coordination center with its neighbor ligands. Here n represents the number of atoms in each molecule. In case of an octahedral coordinated Fe^{II} complex n=7. The partition function is composed of electronic, magnetic and vibronic contributions in the respective spin states.

- The vibronic contributions to the partition function can be derived from the energy eigenvalues of the harmonic oscillator $E_n = \hbar\omega\left(n+\frac{1}{2}\right)$ as [18, 29]:

$$Z_S^v = \prod_{i=1}^{3n-6} \frac{e^{\left(\frac{-h\nu_{S,i}}{2kT}\right)}}{1-e^{\left(\frac{-h\nu_{S,i}}{2kT}\right)}} = e^{\left(-\sum_{i=1}^{3n-6}\frac{h\nu_{S,i}}{2kT}\right)} \prod_{i=1}^{3n-6} \frac{1}{1-e^{\left(\frac{h\nu_{S,i}}{2kT}\right)}} \tag{7}$$

where S indicates the respective Spin State

- The electronic increment to the partition function [30] is based on the respective degenerations of the orbitals and the energy term:

$$Z_s^{el} = g_S^e e^{-\frac{(E_S^e - E_0)}{k_B T}} = g_S^e e^{-\frac{(\Delta - 2J\langle\sigma\rangle)}{k_B T}} \tag{8}$$

- As derived in [24] the magnetic contribution to the partition function results as:

$$Z_{mag} = \frac{\sinh\left(x\left(S+\frac{1}{2}\right)\right)}{\sinh\left(x/2\right)} \qquad (9)$$

Thus the whole partition function can be re-written as:

$$Z = Z_{vib} + Z_{el} + Z_{magn} = e^{\left(-\sum\limits_{i=1}^{3n-6}\frac{h\nu_{S,i}}{2kT}\right)}\prod\limits_{i=1}^{3n-6}\frac{1}{1-e^{\left(\frac{h\nu_{S,i}}{2kT}\right)}} + g_S^e e^{-\frac{(\Delta-2J\langle\sigma\rangle)}{k_BT}} + \frac{\sinh\left(x\left(S+\frac{1}{2}\right)\right)}{\sinh\left(x/2\right)} \qquad (10)$$

For equilibrium between HS and LS state the equilibrium constant K can be written as a function of the Gibbs energy:

$$K_{eq} = \frac{x_{HS}}{x_{LS}} = e^{\frac{\Delta G}{kT}} = e^{\ln(z_{mag}^{HS} z_{el}^{HS} z_{vib}^{HS})-\ln(z_{mag}^{LS} z_{el}^{LS} z_{vib}^{LS})} = \frac{Z^{HS}}{Z^{LS}} \qquad (11)$$

Inserting the different increments of the partition functions and summing up the energies of the zero point vibrations over all vibration modes yields to [18]:

$$K_{eq} = \frac{x_{HS}}{x_{LS}} = r_{eff} e^{\frac{(-\Delta_{eff}+2J\langle\sigma\rangle)}{k_BT}} \text{ with the so called "effective" parameters: } r_{eff} = \frac{g_e^{HS}}{g_e^{LS}}\prod\limits_{i=1}^{3n-6}\frac{1-e^{\left(\frac{-h\nu_{LS,i}}{kT}\right)}}{1-e^{\left(\frac{-h\nu_{HS,i}}{kT}\right)}}$$

and $\Delta_{eff} = \Delta_0 + (\varepsilon_v^{HS} - \varepsilon_v^{HS})$ including the mean value of the fictitious spin operator [31] $\langle\sigma\rangle = 2n_{HS}-1$

In order to obtain a solution for the transition temperature $T_{1/2}$ several approximations are necessary. Due to the fact that r_{eff} is a (comparing LS and HS-state quite strongly) temperature dependent quantity one replaces the different (3n-6) frequencies of the vibrational modes (which are all nearly constant in HS and LS or change a little) by a mode with a big shift between HS $\bar{\nu}_{HS}$ and LS $\bar{\nu}_{LS}$ (such as the Fe-N stretching mode) [18].

Under the approximation of 3n-6 equal vibration modes (i.e. Fe-N stretching mode) the effective degeneration ratio is written as:

$$Z_{vib} = r_{eff} = \frac{g_e^{HS}}{g_e^{LS}} \left(\frac{1 - e^{\left(\frac{h\bar{\nu}_{LS}}{kT}\right)}}{1 - e^{\left(-\frac{h\bar{\nu}_{HS}}{kT}\right)}} \right)^{3n-6} \tag{12}$$

and the energies of the zero point vibrations, summed up over all vibration modes reduce to:

$$\bar{\varepsilon}_{HS}^v - \bar{\varepsilon}_{LS}^v = \frac{1}{2} \left(\sum_i^{3n-6} h\bar{\nu}_{HS} - \sum_i^{3n-6} h\bar{\nu}_{LS} \right) = \frac{3n-6}{2} h\left(\bar{\nu}_{HS} - \bar{\nu}_{LS} \right) \tag{13}$$

This yields to an equilibrium constant:

$$K_{eq} = \frac{Z_{mag}^{HS}}{Z_{mag}^{LS}} r_{eff} e^{\frac{-\left(\Delta_0 - 2J\langle\sigma\rangle - \frac{3n-6}{2} h(\bar{\nu}_{HS} - \bar{\nu}_{LS}) \right)}{k_B T}} =$$

$$\frac{\sinh\left(\frac{g\mu_B B}{k_B T_{1/2}(B)} \left(S_{HS} + \frac{1}{2} \right) \right)}{\sinh\left(\frac{g\mu_B B}{k_B T_{1/2}(B)} \left(S_{LS} + \frac{1}{2} \right) \right)} \frac{g_e^{HS}}{g_e^{LS}} \left(\frac{1 - e^{-\frac{h\bar{\nu}_{LS}}{k_B T_{1/2}(B)}}}{1 - e^{-\frac{h\bar{\nu}_{HS}}{k_B T_{1/2}(B)}}} \right)^{3n-6} e^{\frac{-\left(\frac{\Delta H}{N_A} \right)}{k_B T_{1/2}(B)}} \tag{14}$$

In case of spin equilibrium, with $K_{eq} = 1$ we can calculate the field dependency of the equilibrium temperature $T_{1/2}(B)$, taking the relations between the microscopic parameters Δ_{eff} and r_{eff} and the thermodynamic quantities ΔS and ΔH through: $\Delta S = \ln r_{eff}$, $\Delta H = N_A \Delta_{eff} = N_A (\Delta_0 + (\varepsilon_{HS}^v - \varepsilon_{LS}^v))$ into account.

Nevertheless a value of the interaction constant J is needed for simulating the whole spin transition curve. The $\lim_{T \to 0} K_{eq}$ yields to the necessary information about the value of J and yields for a "true" LS state (up to 100K with $x_{HS} = 0$) for the complex $[Fe(ptz)_6(BF_4)_2]$ to: J=11,8K [24]. Figure 4 depicts the effect of different magnetic fields on the spin transition – again a downward shift of the transition temperature.

Up to our knowledge there is no analytic solution for this equation so that the solution was obtained numerically.

To explore the influence of the interaction constant on the transition calculations with a varying J have been carried out, which are presented in fig. 5 [32].
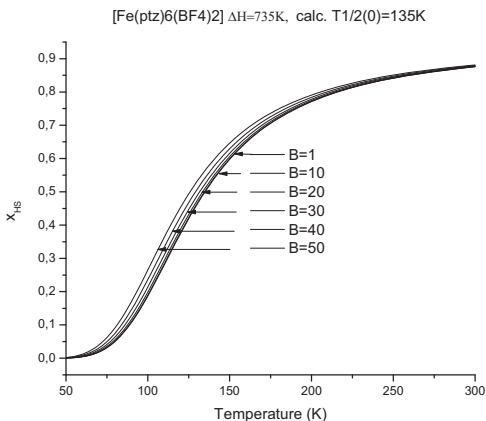

Fig. 4 Simulated Spin Transition curves for different external magnetic fields from 1T to 50T (increasing from right to left). The calculations have been made for $[Fe(ptz)_6(BF_4)_2]$ with ΔH=735K, T1/2=135K, J= 11.8K and $v_{HS} = 167cm^{-1}$ and $v_{LS} = 412cm^{-1}$ [29]. The applied magnetic field induces a downward shift of the transition temperature.
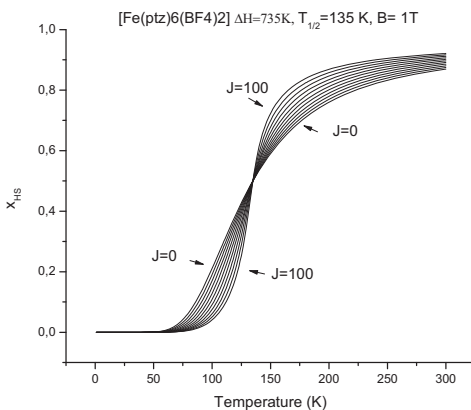

Fig. 5 Simulated Spin Transition curves with different interaction constants J from 0K to 100K, increasing by steps of 10K (from no to large cooperativity). The calculations have been made for $[Fe(ptz)_6(BF_4)_2]$ with the parameter set: ΔH=735K, T1/2=135K, B= 1T and $\bar{v}_{HS} = 167cm^{-1}$ and $\bar{v}_{LS} = 412cm^{-1}$ [29].

3. Discussion and comparison with experimental data

In the presented work we have combined two already existing models: on the one hand an Ising like model including a Zeeman contribution, as extensively studied in [19, 21]. On the other hand a model considering molecular vibrations, which clearly affect the partition function and which are with no doubt the driving motor for the thermal Spin Crossover [29, 33].

The main goal was the elaboration of the field dependency of the spin transition (fig.1, 2 and 4). In thermal expansion measurements one obtains a downward shift of the transition temperature of $\delta T_{1/2} = 0.2K$ for an external magnetic field of 9T for the complex $[Fe(ptz)_6(BF_4)_2]$ (fig.6) [2]. The calculations for this complex yielded to a shift of $\delta T_{1/2} = 0.5K$ for a field of 9T [24], which is in excellent agreement to the experimental results [2].
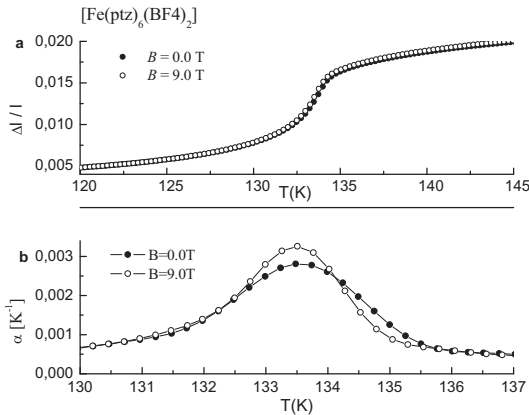

Fig. 6 Thermal expansion measurement for a pressed pellet of polycrystalline $[Fe(ptz)_6(BF_4)_2]$: a) $\Delta l / l$ measurement in a zerofield (filled dots) and in a field of B=9T (open dots). The relative change in length from LS to HS is about 2.0 % and the downward shift of the transition temperature is 0.2K. b) The linear expansion coefficient α for $[Fe(ptz)_6(BF_4)_2]$ is displayed for the respective fields. Here the influence of the magnetic field is even more apparent. A clear influence of the magnetic field on the transition curve can be seen in a) and b) [2].

The capacitive cell used for the thermal expansion measurements is described in [34]. The experimental error in Δl/l of this cell in the used temperature range was far smaller than the symbol size in fig. 6 (approx. 0.5%). One should note that it is quite difficult to determine the

absolute error of the respective sample, as the sample length varies slightly for each measurement due to small cracks inside the samples.

Due to the additive character of our model one can simply add up the different contributions of the partition functions and combine these two models (see equation(10)). Obviously this model is more complex due to the fact, that more experimental parameters are considered (enthalpy, interaction constant J, Fe-N stretching mode). Nevertheless the applicability still is restricted. The approximation made in (12) is not valid for bridging ligands (like the 4 di-tetrazole) or for any kind of 3D network forming complexes as observed in several systems [25, 27]. Only for isolated molecules like $[Fe(ptz)_6(BF_4)_2]$ ligands might be considered as point shaped without loss of generality. To conclude, although the Ising like model is a very simple model it is suitable to calculate characteristic properties of spin transitions, especially including magnetic field dependency. Drawbacks are, that only nearest neighbors are taken into account, that cooperativity is considered only on a limited degree and that there is a need for detailed vibrational data (obtainable from IR- and far-IR measurements as well as from DFT calculations [35]. Nevertheless even the present model yields to a transition curve which is well fitting to the available experimental data [36] (fig.4-5).

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