

Invited Review

Is There a Need for New Models of the Spin Crossover?

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Summary. The existing models of the low-spin to high-spin transition (spin crossover) are briefly reviewed. Experimental data pointing to a need of new models are displayed. A statistical model with the distribution of the solid-state cooperativeness is outlined. A modeling is shown as well as its application to a spin crossover system $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2 \cdot 0.25\text{H}_2\text{O}$. This shows an abrupt spin crossover at temperature as high as 403 K with a hysteresis width of 12 K. The angled walls of the hysteresis loop can be followed by the outlined statistical model.

Keywords. Spin crossover; Domain model; Solution model; Statistical model; Cooperativeness.

Introduction

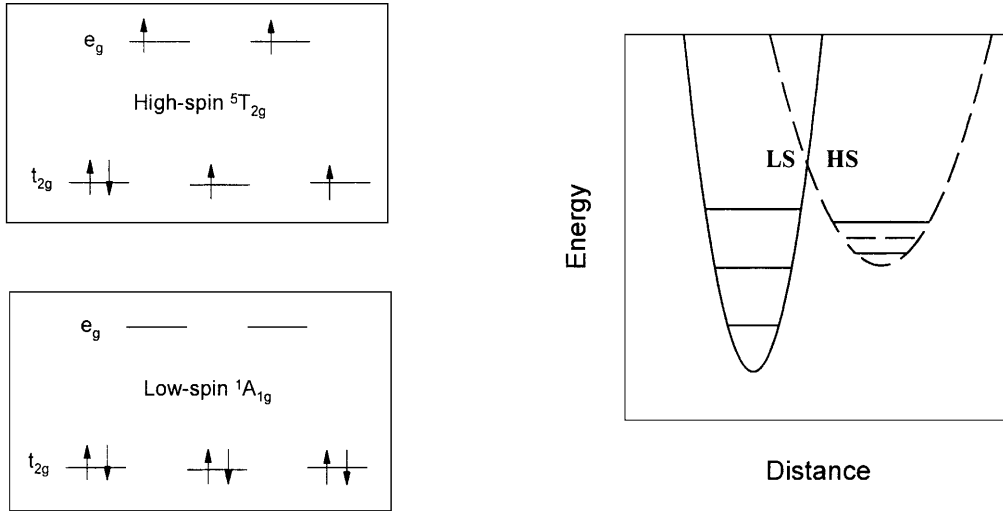
Several transition metal complexes, especially those with d^4 to d^7 metal ion configuration, can exist either in the low-spin (LS) or high-spin (HS) states. Exceptionally, they can exist also in an intermediate-spin (IS) state. When the high-spin state is the ground-one, this is not altered by the temperature variation. However, when the ground state is the low-spin, a spin transition to the high-spin state can occur (Fig. 1).

There are two conditions for the spin crossover:

1. the enthalpy change (that includes the electronic and the vibrational contribution) should be positive

$$\Delta H = (E_{\text{HS}}^{\text{el}} + \varepsilon_{\text{HS}}^{\text{vib}}) - (E_{\text{LS}}^{\text{el}} + \varepsilon_{\text{LS}}^{\text{vib}}) > 0 \quad (1)$$

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Electron configuration for LS and HS of an octahedral d^6 system

Total energy (adiabatic potential)

Fig. 1. Circumstances of the spin crossover

2. the entropy change (in the first, very crude approximation given by the electronic state degeneracy g^{el}) should be positive

$$\Delta S = k \ln g_{\text{HS}}^{\text{el}} - k \ln g_{\text{LS}}^{\text{el}} = k \ln \left(\frac{g_{\text{HS}}^{\text{el}}}{g_{\text{LS}}^{\text{el}}} \right) > 0 \quad (2)$$

Consequently the *Gibbs* energy $\Delta G = \Delta H - T \cdot \Delta S$ passes through the zero at the transition (critical) temperature (Fig. 2).

$$T_c = \Delta H / \Delta S \quad (3)$$

and the *vant' Hoff* plot, *i.e.* $\ln K$ vs. $(1/T)$, is a straight line intercepting zero at the transition temperature

$$\ln K = \ln \frac{x_{\text{HS}}}{x_{\text{LS}}} = \ln \frac{x_{\text{HS}}}{1 - x_{\text{HS}}} \quad (4)$$

$$\ln K = -\frac{\Delta G}{RT} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (5)$$

The slope of the *vant' Hoff* plot determines the enthalpy change whereas the intercept with the abscissa (when $1/T \rightarrow 0$) determines the entropy change. All these estimates are valid for a perfect fulfillment of the *Boltzmann* statistics when the deviations (the solid state cooperativeness) are negligible. When the entropy change would vanish, the system does not show the spin crossover: it stays low-spin.

The above requirements are well fulfilled for d^6 systems – iron(II) complexes. The ground low-spin state is $^1A_{1g}$ and this transforms to the high-spin excited state $^5T_{2g}$. The enthalpy change is positive owing to the promotion of electrons from

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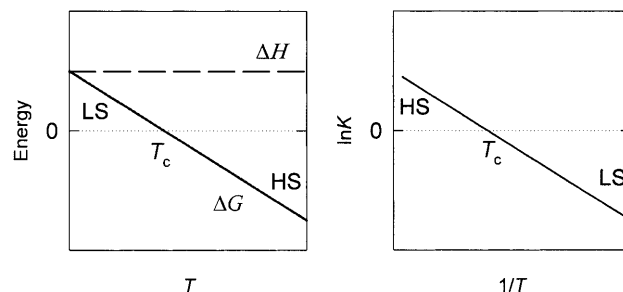


Fig. 2. Temperature variation of the *Gibbs* energy (left) and the *van't Hoff* plot (right) for a spin crossover system

Table 1. Experimental monitoring of the spin crossover

Experimental method	Monitored property LS \xrightarrow{T} HS
Magnetic measurements (MM)	magnetic susceptibility, effective magnetic moment, low \xrightarrow{T} high
<i>Mössbauer</i> spectra (MS)	quadrupole splitting, low \xrightarrow{T} high for Fe(II)
Vibrational spectra (IR)	M-L stretching wavenumber, high \xrightarrow{T} low
Electron spectra (ES)	excitation energy, low \xrightarrow{T} high
Calorimetric measurements (DSC)	heat capacity, low \xrightarrow{T} high, a lambda-peak
X-ray diffraction	cell parameters, volume of the unit cell, low \xrightarrow{T} high
Extended X-ray absorption fine structure (EXAFS)	metal-ligand distances, low \xrightarrow{T} high
Nuclear magnetic resonance (NMR) in solutions	paramagnetic shift, effective magnetic moment, low \xrightarrow{T} high
Volumetric measurements (VM)	partial molar volume, low \xrightarrow{T} high
Electron spin resonance (ESR)	absorption, g-factor, no ($S = 0$) \xrightarrow{T} yes

non-bonding t_{2g} orbitals to the antibonding e_g -ones (the energetically unfavorable process). The entropy change is positive as $g_{LS}^{el} = 1$ and $g_{HS}^{el} = 3 \times 5$. When the orbital degeneracy is removed on symmetry lowering, the high-spin state ${}^5A_{1g}$ will possess $g_{HS}^{el} = 5$ giving rise to the lowest estimate of $\Delta S = R \ln 5 = 13.6 \text{ JK}^{-1} \text{ mol}^{-1}$.

The spin crossover can be monitored by several experimental techniques as listed in Table 1. However the monitored properties can be transformed to a common basis that is the high-spin mole fraction x_{HS} . For more deep information the reader should consult the literature [1–9].

Hamiltonian and Kets

The Hamiltonian appropriate for the spin crossover system is a two-level *Ising*-like Hamiltonian of the form

$$\hat{H} = (\Delta_0/2)\hat{\sigma} - J\langle\sigma\rangle\hat{\sigma} \quad (6)$$

where $\hat{\sigma}$ – operator of a fictitious spin that distinguishes between the LS and HS, Δ_0 – site formation energy (energy difference LS–HS), and $J > 0$ – “ferromagnetic”-like or “cooperative” interaction (the sign in front of J is a matter of the

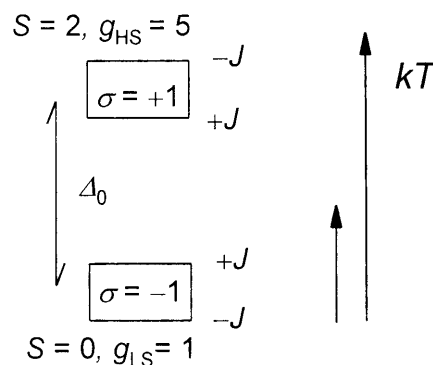


Fig. 3. Energy levels for the *Ising*-like Hamiltonian

convention; this parameter not to be confused with the exchange constant). The thermal average of the fictitious spin $\langle \sigma \rangle$ acts as a mean-field term and it is

$$\langle \sigma \rangle = \frac{\sum_i \sigma_i \exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} \quad (7)$$

It scales the high-spin mole fraction as follows

$$x_{\text{HS}} = (1 + \langle \sigma \rangle)/2 \quad (8)$$

The kets act as follows

$$\hat{\sigma}|-1\rangle = -1 \quad (9)$$

$$\hat{\sigma}|+1\rangle = +1 \quad (10)$$

and they yield two energy levels (Fig. 3)

$$E_1(\sigma = -1) = -\Delta_0/2 + J\langle \sigma \rangle \quad (11)$$

$$E_2(\sigma = +1) = +\Delta_0/2 - J\langle \sigma \rangle \quad (12)$$

The key problem of the *Ising*-like model and its variants is the determination of the thermal average of the fictitious spin. There are two routes for such a purpose.

- 1) The equilibrium constant of a unimolecular reaction $\text{LS} \leftrightarrow \text{HS}$ is expressed through the reaction *Gibbs* energy

$$K = \exp(-\Delta_r G/RT) = \exp[-(G_{T,\text{HS}}^0 - G_{T,\text{LS}}^0)/RT] \quad (13)$$

On ignoring the difference between ΔF and ΔG for a solid sample (equivalent but distinguishable particles are assumed)

$$G \approx F = -RT \ln z \quad (14)$$

where

$$z_{\text{LS}} = z_{\text{LS}}^{\text{el}} \cdot z_{\text{LS}}^{\text{vib}} \quad (15)$$

stands for the partition function of the given reactant (LS) and product (HS), respectively. Then

$$K = \frac{z_{\text{HS}}^{\text{el}} \cdot z_{\text{HS}}^{\text{vib}}}{z_{\text{LS}}^{\text{el}} \cdot z_{\text{LS}}^{\text{vib}}} \quad (16)$$

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On the other hand there is

$$K = \frac{x_{HS}}{x_{LS}} = \frac{x_{HS}}{1 - x_{HS}} = \frac{1 + \langle \sigma \rangle}{1 - \langle \sigma \rangle} \quad (17)$$

from where one gets the equation

$$\langle \sigma \rangle = \frac{-1 + K}{+1 + K} \quad (18)$$

- 2) A direct application of the *Boltzmann* statistics for two possible values of the fictitious spin yields (the total partition function is applied)

$$\langle \sigma \rangle = \frac{(-1)z_{LS}^{\text{el}} \cdot z_{LS}^{\text{vib}} + (+1)z_{HS}^{\text{el}} \cdot z_{HS}^{\text{vib}}}{z_{LS}^{\text{el}} \cdot z_{LS}^{\text{vib}} + z_{HS}^{\text{el}} \cdot z_{HS}^{\text{vib}}} = \frac{-1 + K}{+1 + K} \quad (19)$$

where the expression for K is identical as above.

For the two-level *Ising*-like model the electronic partition functions are

$$z_{LS}^{\text{el}} = g_{LS}^{\text{el}} \exp[-(-\Delta_0/2 + J\langle \sigma \rangle)/kT] \quad (20)$$

$$z_{HS}^{\text{el}} = g_{HS}^{\text{el}} \exp[-(+\Delta_0/2 - J\langle \sigma \rangle)/kT] \quad (21)$$

and thus the equilibrium constant becomes

$$K = \left(\frac{z_{HS}^{\text{vib}} \cdot g_{HS}^{\text{el}}}{z_{LS}^{\text{vib}} \cdot g_{LS}^{\text{el}}} \right) \exp[-(\Delta_0 - 2J\langle \sigma \rangle)/kT] \quad (22)$$

In the simplest case – the *model A* – a constant preexponential factor is assumed and termed the effective degeneracy ratio

$$r_{\text{eff}} = \left(\frac{z_{HS}^{\text{vib}} \cdot g_{HS}^{\text{el}}}{z_{LS}^{\text{vib}} \cdot g_{LS}^{\text{el}}} \right) \quad (23)$$

Then the implicit equation is to be obeyed

$$\langle \sigma \rangle = \frac{-1 + r_{\text{eff}} \exp[-(\Delta_0 - 2J\langle \sigma \rangle)/kT]}{+1 + r_{\text{eff}} \exp[-(\Delta_0 - 2J\langle \sigma \rangle)/kT]} \quad (24)$$

and this needs to be solved through an iterative procedure. The free parameters of the model are: r_{eff} , Δ_0 and J . These microscopic parameters are related to the thermodynamic quantities through

$$\Delta S = R \ln r_{\text{eff}} \quad (25)$$

$$\Delta H = N_A \Delta_0 \quad (26)$$

The involvement of the molecular vibrations – the *model B* – proceeds through the vibration partition function

$$\begin{aligned} z_{LS}^{\text{vib}} &= \prod_{i=1}^{3n-6} \frac{\exp(-hv_{LS,i}/2kT)}{1 - \exp(-hv_{LS,i}/kT)} \\ &= \exp \left[\sum_{i=1}^{3n-6} (hv_{LS,i}/2kT) \right] \prod_{i=1}^{3n-6} \frac{1}{1 - \exp(-hv_{LS,i}/kT)} \end{aligned} \quad (27)$$

and analogously for the HS molecules. Then the equilibrium constant becomes expressed as

$$K = \left(\frac{g_{\text{HS}}^{\text{el}}}{g_{\text{LS}}^{\text{el}}} \right) \left[\prod_{i=1}^{3n-6} \frac{1 - \exp(-hv_{\text{LS},i}/kT)}{1 - \exp(-hv_{\text{HS},i}/kT)} \right] \exp\{-[\Delta_0 + (\varepsilon_{\text{HS}} - \varepsilon_{\text{LS}}) - 2J\langle\sigma\rangle]/kT\} \quad (28)$$

where the energy of the zero-point vibration was summed up over all vibration modes

$$\varepsilon_{\text{LS}} = \frac{1}{2} \sum_{i=1}^{3n-6} hv_{\text{LS},i} \quad (29)$$

and analogously for the HS.

There are two approximations to the model:

1. The relevant (low-energy) modes are averaged to give $h\bar{v}_{\text{LS}}$ and $h\bar{v}_{\text{HS}}$; then

$$K = \left(\frac{g_{\text{HS}}^{\text{el}}}{g_{\text{LS}}^{\text{el}}} \right) \left[\frac{1 - \exp(-h\bar{v}_{\text{LS}}/kT)}{1 - \exp(-h\bar{v}_{\text{HS}}/kT)} \right]^{3n-6} \exp\{-[\Delta_0 + (3n-6)/2(h\bar{v}_{\text{HS}} - h\bar{v}_{\text{LS}}) - 2J\langle\sigma\rangle]/kT\} \quad (30)$$

2. In the limit of low vibration frequencies $hv \ll kT$ is fulfilled. Then the exponentials can be expanded into a *Taylor* series and their truncation after the second term yields

$$K = \left(\frac{g_{\text{HS}}^{\text{el}}}{g_{\text{LS}}^{\text{el}}} \right) \left[\frac{h\bar{v}_{\text{LS}}}{h\bar{v}_{\text{HS}}} \right]^{3n-6} \exp\{-[\Delta_0 + (3n-6)/2(h\bar{v}_{\text{HS}} - h\bar{v}_{\text{LS}}) - 2J\langle\sigma\rangle]/kT\} \quad (31)$$

and now

$$r_{\text{eff}} = \left(\frac{g_{\text{HS}}^{\text{el}}}{g_{\text{LS}}^{\text{el}}} \right) \left[\frac{h\bar{v}_{\text{LS}}}{h\bar{v}_{\text{HS}}} \right]^{3n-6} \quad (32)$$

$$\Delta_{\text{eff}} = \Delta_0 + (3n-6)/2(h\bar{v}_{\text{HS}} - h\bar{v}_{\text{LS}}) \quad (33)$$

For hexacoordinate Fe(II) complexes 15 vibrational modes of the chromophore are relevant and the experimental data show that $(h\bar{v}_{\text{LS}}) \approx 1.5(h\bar{v}_{\text{HS}})$. Then the rough estimate is $r_{\text{eff}} = 5(1.5)^{15} = 2189$ and consequently $\Delta S = R \ln r_{\text{eff}} = 8.3 \times \ln(2189) = 64 \text{ J K}^{-1} \text{ mol}^{-1}$.

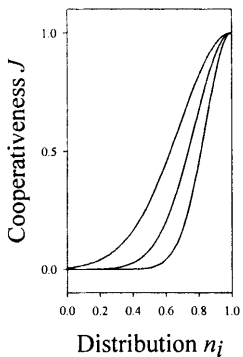
Final Formulae and Modeling

The final formulae of the *Ising*-like model of the spin crossover are collected in Table 2. A modeling is given by Fig. 4 and the following important findings become evident.

1. An increase of ΔH (at constant ΔS) raises the transition temperature.
2. An increase of ΔH , and simultaneous accommodation of ΔS to keep the transition temperature $T_c = \Delta H/\Delta S$ constant, causes an increased abruptness of the conversion curve $x_{\text{HS}} = f(T)$.

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Table 2. Formulae of the *Ising*-like models for mononuclear spin crossover systems

Derivation	Hamiltonian $\hat{H} = (\Delta_0/2)\hat{\sigma} - J\langle\sigma\rangle\hat{\sigma}$ in mean-field approximation Δ_0 – site formation energy (energy difference $E_{\text{HS}} - E_{\text{LS}}$) $J > 0$ – “ferromagnetic”-like or “cooperative” interaction
Implicit equation to be iterated	$\langle\sigma\rangle_T = \frac{-1 + f(\langle\sigma\rangle_T)}{1 + f(\langle\sigma\rangle_T)}$
High-spin mole fraction	$x_{\text{HS}} = (1 + \langle\sigma\rangle)/2$
Model A (<i>Ising</i> -like)	$f^{(\text{A})} = r_{\text{eff}} \exp[-(\Delta_0 - 2J\langle\sigma\rangle_T)/kT]$ $r_{\text{eff}} = r_{\text{el}} r_{\text{vib}} > 5$ – effective degeneracy ratio; $r_{\text{el}} = g_{\text{HS}}^{\text{el}}/g_{\text{LS}}^{\text{el}}$ $\Delta S = R \ln r_{\text{eff}}$; $\Delta H = N_{\Lambda} \Delta_0$
Model B (<i>Ising</i> -like & vibrations)	$f^{(\text{B})} = r_{\text{eff}}(T) \times \exp\{-[\Delta_{\text{eff}} - 2J\langle\sigma\rangle_T]/kT\}$ $r_{\text{eff}}(T) = \frac{g_{\text{HS}}^{\text{el}}}{g_{\text{LS}}^{\text{el}}} \left[\frac{1 - \exp(h\bar{v}_{\text{LS}}/kT)}{1 - \exp(h\bar{v}_{\text{HS}}/kT)} \right]^m$ $\Delta_{\text{eff}} = \Delta_0 + m(h\bar{v}_{\text{HS}} - h\bar{v}_{\text{LS}})/2$ m – active modes ($m = 15$ for a hexacoordinate complex) $h\bar{v}_{\text{HS}}$ and $h\bar{v}_{\text{LS}}$ – averaged vibration energies
Model C (<i>Ising</i> -like & domains)	$f^{(\text{C})} = \exp\{-[\Delta H - T\Delta S - \gamma(2x_{\text{HS}} - 1)]n/RT\}$ $= \exp\{-[\Delta_0 - kT \ln r_{\text{eff}} - 2J\langle\sigma\rangle_T]n/kT\}$ n – optimum domain size
Model D (<i>Ising</i> -like & parameter distribution)	$f_i^{(\text{D})} = \exp\{-[\Delta_0 - kT \ln r_{\text{eff}} - 2n_i J\langle\sigma_i\rangle_T]/kT\}$ $x_i = (1 + \langle\sigma_i\rangle_T)/2$ $w_i \approx \exp[-(n_i - n_{\text{opt}})^2/\delta]$ – Gaussian distribution
	$x_{\text{HS}} = \frac{\left[\sum_{i=1}^{\text{Mesh}} w_i \cdot x_i \right]}{\left[\sum_{i=1}^{\text{Mesh}} w_i \right]}$ – a statistical average
	
Equilibrium constant	$\ln K = \ln \frac{x_{\text{HS}}}{1 - x_{\text{HS}}} = -[\Delta H - T\Delta S + \gamma(1 - 2x_{\text{HS}})]n/RT$

3. The increased domain size raises the abruptness of the conversion curve.
4. The increased cooperativeness causes a non-linearity near T_c (inverse S-shaped curvature) in the *van't Hoff* plot. above the critical value of $J > kT_c$ a hysteresis is obtained: the conversion curves on the heating and the cooling directions have different profiles.
5. The role of the vibrations makes a non-linearity of the *van't Hoff* line at low temperature; in an extreme case the system can return to the high-spin state on cooling.

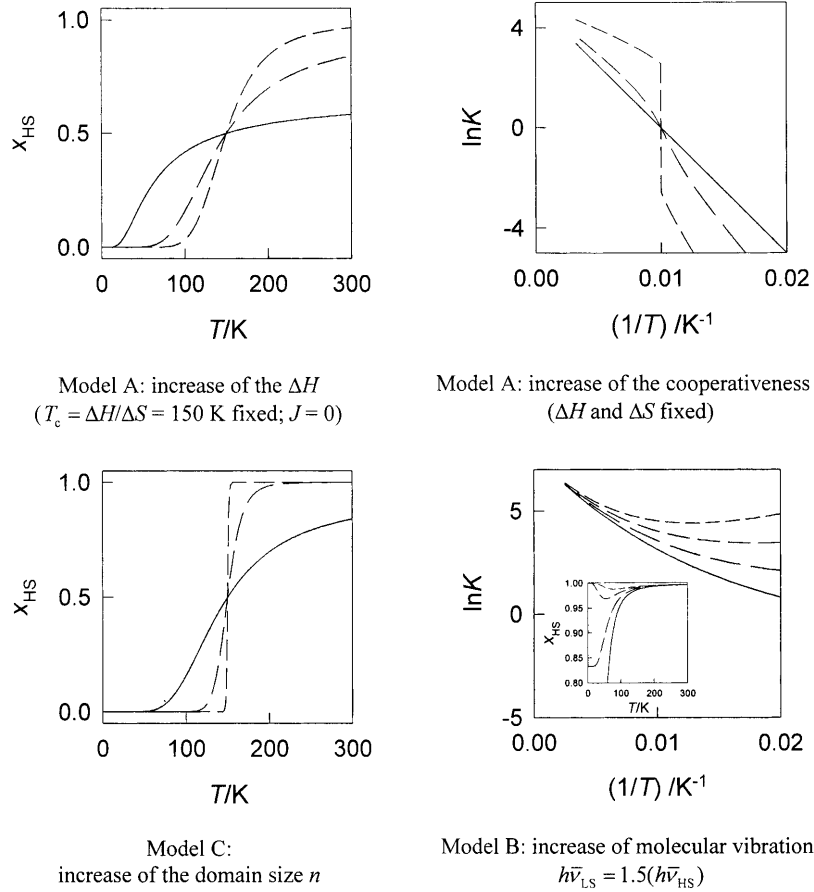


Fig. 4. Modeling of the spin crossover with the *Ising*-like model. Individual lines (full, long dashed, short dashed) correspond to the increase of a varied parameter

Extensions of the *Ising*-Like Model

Two basic derivations for the spin crossover models were presented in literature:

- 1) former thermodynamic approach starting with the mixing entropy, postulated interaction terms, the *Gibbs* energy and its stationery with respect to x_{HS} ;
- 2) a novel microscopic approach starting with the postulated Hamiltonian, derived energy levels, partition function, and the thermodynamic properties.

Thermodynamic Approach

- a) The mixing entropy is expressed through the statistical probability of the state. In an assembly of N molecules there is a number of $x_{HS}N$ molecules in the HS state and the residual number of $(1 - x_{HS})N$ molecules in the LS state. The mixing entropy S_{mix} accounts for the fact that there are several ways of

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distributing the LS and HS molecules within the assembly of N molecules

$$\begin{aligned} S_{\text{mix}} &= k \ln W = k \ln \frac{N!}{(xN)![(1-x)N]!} \\ &= k\{N \ln N - xN \ln(xN) - (1-x)N \ln[(1-x)N]\} \\ &= -kN\{x \ln x + (1-x) \ln(1-x)\} \end{aligned} \quad (34)$$

where we applied the *Stirling* formula for the factorials ($x \equiv x_{\text{HS}}$ for the sake of clarity).

- b) When the formation of domains of like spin is assumed then the number of molecules per domain is $n = N/D$ if the domains have a uniform size. The mixing entropy alters to

$$S_{\text{mix}} = k \ln \frac{D!}{(xD)![(1-x)D]!} = -kD\{x \ln x + (1-x) \ln(1-x)\} \quad (35)$$

For one mole ($N = N_{\text{A}}$) of molecules the molar mixing entropy can be rewritten as

$$S_{\text{mix}} = -(R/n)\{x \ln x + (1-x) \ln(1-x)\} \quad (36)$$

where $R = N_{\text{A}}k$ holds true.

- c) The intermolecular interaction term I_x can be expressed in the general form

$$I_x = I_{\text{LL}}(1-x)^2 + 2I_{\text{LH}}x(1-x) + I_{\text{HH}}x^2 = J_0 + J_1x + J_2x^2 \quad (37)$$

where I_{LL} , I_{LH} , I_{HH} refer to interactions between LS–LS, LS–HS and HS–HS pairs, respectively. Then $J_0 = I_{\text{LL}}$, $J_1 = 2(I_{\text{LH}} - I_{\text{LL}})$, and $J_2 = I_{\text{LL}} + I_{\text{HH}} - 2I_{\text{LH}}$.

- d) The molar *Gibbs* energy can be constructed from the following contributions

$$G_x = xG_{\text{HS}} + (1-x)G_{\text{LS}} - TS_{\text{mix}} + I_x \quad (38)$$

where G_{HS} (G_{LS}) is the molar *Gibbs* energy for the HS (LS) molecules.

- e) The condition for the equilibrium demands

$$\left(\frac{\partial G_x}{\partial x}\right)_{T,p} = G_{\text{HS}} - G_{\text{LS}} + (R/n)T \ln\left(\frac{x}{1-x}\right) + J_1 + 2J_2x = 0 \quad (39)$$

from where one gets the final, implicit equation for the high-spin mole fraction

$$x = \frac{1}{1 + \exp[n(\Delta H - T\Delta S + J_1 + 2J_2x)/RT]} \quad (40)$$

The last, very general equation – *model C* has many links to more approximate models as reviewed by Table 3.

The basic assumption of the *solution model* is that the interaction term involves the cooperativeness γ through the form

$$I_x = \gamma x(1-x) \quad (41)$$

This formula has its origin in the intercentre interaction

$$I_x = J_0 + J_1x + J_2x^2 = I_{\text{LL}} + 2(I_{\text{LH}} - I_{\text{LL}})x + (I_{\text{LL}} + I_{\text{HH}} - 2I_{\text{LH}})x^2 \quad (42)$$

Table 3. Review of the spin crossover models

Model	Parameters $I_x = J_0 + J_1x + J_2x^2$	$x = f(T)$
1. Thermodynamic models		
Domain model <i>Sorai & Seki</i> [10]	$J_1 = J_2 = 0$	$x = 1/\{1 + \exp(n\Delta G/RT)\}$
Solution model <i>Drickamer</i> [11]	$J_1 = -J_2 = \gamma;$ $I_x = \gamma x(1-x)$	$x = 1/\{1 + \exp[(\Delta G + \gamma - 2\gamma x)/RT]\}$
Interaction model <i>McGarvey et al.</i> [12]	$J_1 \neq 0, J_2 \neq 0$	$x = 1/\{1 + \exp[(\Delta G + J_1 + 2J_2x)/RT]\}$
<i>Zimmermann & König</i> [13]	$J_1 = 0, J_2 = -J$	$x = 1/\{1 + \exp[(\Delta - RT \ln Z - 2Jx)/RT]\}$
<i>Spiering et al.</i> [14, 15]	$J_1 = \Delta_x, J_2 = -\Gamma_x$	$x = 1/\{1 + \exp[(\Delta G + \Delta_x - 2\Gamma_x x)/RT]\}$
Interaction & domain [16]	$J_1 \neq 0, J_2 \neq 0$	$x = 1/\{1 + \exp[n(\Delta H - T\Delta S + J_1 + 2J_2x)/RT]\}$
Interaction model for two-step and binuclear systems [35, 28]		
2. Microscopic models		
<i>Ising-like</i> [17, 18]; model A	$\hat{I}_\sigma = -J\langle\sigma\rangle\hat{\sigma}$ $\langle\sigma\rangle = 2x - 1$	$x = 1/\{1 + \exp[(\Delta_0 - kT \ln r_{\text{eff}} - 2J(2x - 1))/kT]\}$
<i>Ising-like with vibrations</i> [19]; model B	$\hat{I}_\sigma = -J\langle\sigma\rangle\hat{\sigma}$ $\langle\sigma\rangle = 2x - 1$	$x = 1/\{1 + \exp[(\Delta_{\text{eff}} - kT \ln r_{\text{eff},T} - 2J(2x - 1))/kT]\}$ $r_{\text{eff},T} = \frac{g_{\text{HS}}^{\text{el}}}{g_{\text{LS}}^{\text{el}}} \left[\frac{1 - \exp(h\bar{v}_{\text{LS}}/kT)}{1 - \exp(h\bar{v}_{\text{HS}}/kT)} \right]^m$ $\Delta_{\text{eff}} = \Delta_0 + m(h\bar{v}_{\text{HS}} - h\bar{v}_{\text{LS}})/2$
<i>Ising-like & domain model;</i> model C	$\hat{I}_\sigma = -J\langle\sigma\rangle\hat{\sigma}$ $\langle\sigma\rangle = 2x - 1$	$x = 1/\{1 + \exp[n(\Delta_{\text{eff}} - kT \ln r_{\text{eff},T} - 2J(2x - 1))/kT]\}$
Parameter distribution [20]; model D	$x_{\text{HS}} = \left[\sum_{i=1}^{\text{Mesh}} w_i \cdot x_i \right] / \left[\sum_{i=1}^{\text{Mesh}} w_i \right]$	$x_i = 1/\{1 + \exp[(\Delta_{\text{eff}} - kT \ln r_{\text{eff},T} - 2n_i J(2x_i - 1))/kT]\}$
Two-step <i>Ising-like</i> [21]		$\langle\sigma_A\rangle = \frac{-1 + r_{\text{eff}} \exp\{-[\Delta_0 - 2(J_A\langle\sigma_A\rangle + J_{AB}\langle\sigma_B\rangle)]/kT\}}{1 + r_{\text{eff}} \exp\{-[\Delta_0 - 2(J_A\langle\sigma_A\rangle + J_{AB}\langle\sigma_B\rangle)]/kT\}}$ $\langle\sigma_B\rangle = \frac{-1 + r_{\text{eff}} \exp\{-[\Delta_0 - 2(J_B\langle\sigma_B\rangle + J_{AB}\langle\sigma_A\rangle)]/kT\}}{1 + r_{\text{eff}} \exp\{-[\Delta_0 - 2(J_B\langle\sigma_B\rangle + J_{AB}\langle\sigma_A\rangle)]/kT\}}$
1D- <i>Ising-like</i> [29]		
<i>Ising-like for binuclear compounds</i> [22]	$x = (2 + \langle\sigma_A\rangle + \langle\sigma_B\rangle)/4$	$\langle\sigma_A\rangle = [-\exp(-E_1/kT) - r_{\text{eff}} \exp(-E_2/kT) + r_{\text{eff}} \exp(-E_3/kT) + r_{\text{eff}}^2 \exp(-E_4/kT)]/Z_0$ $\langle\sigma_B\rangle = [-\exp(-E_1/kT) + r_{\text{eff}} \exp(-E_2/kT) - r_{\text{eff}} \exp(-E_3/kT) + r_{\text{eff}}^2 \exp(-E_4/kT)]/Z_0$ $Z_0 = [\exp(-E_1/kT) + r_{\text{eff}} \exp(-E_2/kT) + r_{\text{eff}} \exp(-E_3/kT) + r_{\text{eff}}^2 \exp(-E_4/kT)]$

(continued)

Table 3 (continued)

Model	Parameters $I_x = J_0 + J_1x + J_2x^2$	$x = f(T)$
		$E_1 = -\Delta_0 + (\langle\sigma_A\rangle + \langle\sigma_B\rangle)(J + J') - J_{AB}$ $E_2 = (\langle\sigma_A\rangle - \langle\sigma_B\rangle)(J - J') + J_{AB}$ $E_3 = -(\langle\sigma_A\rangle - \langle\sigma_B\rangle)(J - J') + J_{AB}$ $E_4 = \Delta_0 - (\langle\sigma_A\rangle + \langle\sigma_B\rangle)(J + J') - J_{AB}$
3. Other models		
Vibronic models (electron–phonon coupling) [13, 23]		

yielding the relationship within the solution and/or solution & domain model as follows

$$\frac{\partial I_x}{\partial x} = J_1 + 2J_2x = (J_1 + J_2) - J_2(1 - 2x) = \gamma(1 - 2x) \quad (43)$$

The remainder

$$J_1 + J_2 = I_{HH} - I_{LL} \quad (44)$$

is thought either to vanish or to be absorbed to the effective parameter Δ_{eff} . Then the cooperativeness becomes

$$\gamma = -J_2 = 2I_{LH} - I_{LL} - I_{HH} \quad (45)$$

This means an excess of the interaction energy between the molecules of the different spin relative to the interaction energy of the molecules of the like spin. It is a measure of the tendency for molecules of one type to interact effectively (to be surrounded) by molecules of the like spin.

The solution model, in fact, is fully equivalent to the two-level *Ising*-like model through the correspondence $\gamma/R = 2J$.

Model of a Parameter Distribution

This model has been motivated by the fact that the solid state samples are far from their ideal behavior and some drop in the cooperativeness could be described through a statistical distribution. As the sizable cooperativeness is responsible for the eventual hysteresis, the above effect will manifest itself in the profile of the conversion curve.

The key idea of this *model D* is that the optimum cooperativeness drops as

$$J_i = n_i J \quad (46)$$

Here i is the mesh point, say $1/100$ of the value of $n_{\text{opt}} = 1$. Then the factor entering the implicit equation for $\langle\sigma_i\rangle$ becomes

$$f_i^{(D)} = \exp\{-[\Delta_0 - kT \ln r_{\text{eff}} - 2n_i J \langle\sigma_i\rangle]/kT\} \quad (47)$$

The equation is to be iterated for the given trial set of parameters (Δ_0 , r_{eff} , J), for a given temperature, and for the given mesh point. Moreover, the iteration should

start differently for the data point taken in the heating direction ($\sigma_i^{(0),\uparrow} = -1$ is used as an initial trial) and the cooling direction ($\sigma_i^{(0),\downarrow} = +1$). The statistical average is provided by the formula

$$x_{\text{HS}} = \left[\sum_{i=1}^{\text{Mesh}} w_i \cdot x_i \right] / \left[\sum_{i=1}^{\text{Mesh}} w_i \right] \quad (48)$$

where the weights can be determined from the postulated distribution, e.g. the Gaussian distribution in the form of

$$w_i \approx \exp[-(n_i - n_{\text{opt}})^2 / \delta] \quad (49)$$

Additional parameter δ determines the width of the distribution (Fig. 5):

- 1) for $\delta \approx 0$ a sharp distribution exists and the model D collapses to the model C (or A) with fixed parameters. The hysteresis loop of the conversion curve possesses the rectangular walls.
- 2) The increase of δ manifests itself in angled walls of the hysteresis loop and decreased hysteresis width.
- 3) At the same time the completeness of the spin crossover is lowered and the conversion curve becomes smoother, resembling suppress of the cooperativeness.

The existence of the hysteresis originates in the fact that the *Gibbs* energy possesses two minima at different temperature; the system falls into one of them depending on the history of the heating/cooling regime.

Model for Two-Step Spin Crossover

Some compounds exhibit a spin crossover of the form that the fraction x_{HS} of molecules in the HS state increases with temperature in two steps; a plateau of a few K exists between these steps. This behavior can be explained by considering two sublattices (A and B) containing the same number of molecules [21]. The *Ising*-like Hamiltonians corresponding to the respective lattices, in the mean field approach, are defined as follows

$$\hat{H}_A = (\Delta_0/2)\hat{\sigma}_A - (J_A\langle\sigma_A\rangle + J_{AB}\langle\sigma_B\rangle)\hat{\sigma}_A \quad (50)$$

$$\hat{H}_B = (\Delta_0/2)\hat{\sigma}_B - (J_B\langle\sigma_B\rangle + J_{AB}\langle\sigma_A\rangle)\hat{\sigma}_B \quad (51)$$

where J_A and J_B are the intra-sublattice interaction parameters for A...A and B...B pairs; J_{AB} is the inter-sublattice interaction parameter for A...B pairs. Their positive values mean a ‘‘ferromagnetic-like’’ or cooperative interaction. The mole fractions of the HS state are interrelated through

$$\langle\sigma_A\rangle = 2x_A - 1 \quad (52)$$

$$\langle\sigma_B\rangle = 2x_B - 1 \quad (53)$$

The corresponding eigenvalues are

$$E_{A2} = (\Delta_0/2) - (J_A\langle\sigma_A\rangle + J_{AB}\langle\sigma_B\rangle) \quad (54)$$

$$E_{A1} = -(\Delta_0/2) + (J_A\langle\sigma_A\rangle + J_{AB}\langle\sigma_B\rangle) \quad (55)$$

Need of New Models?

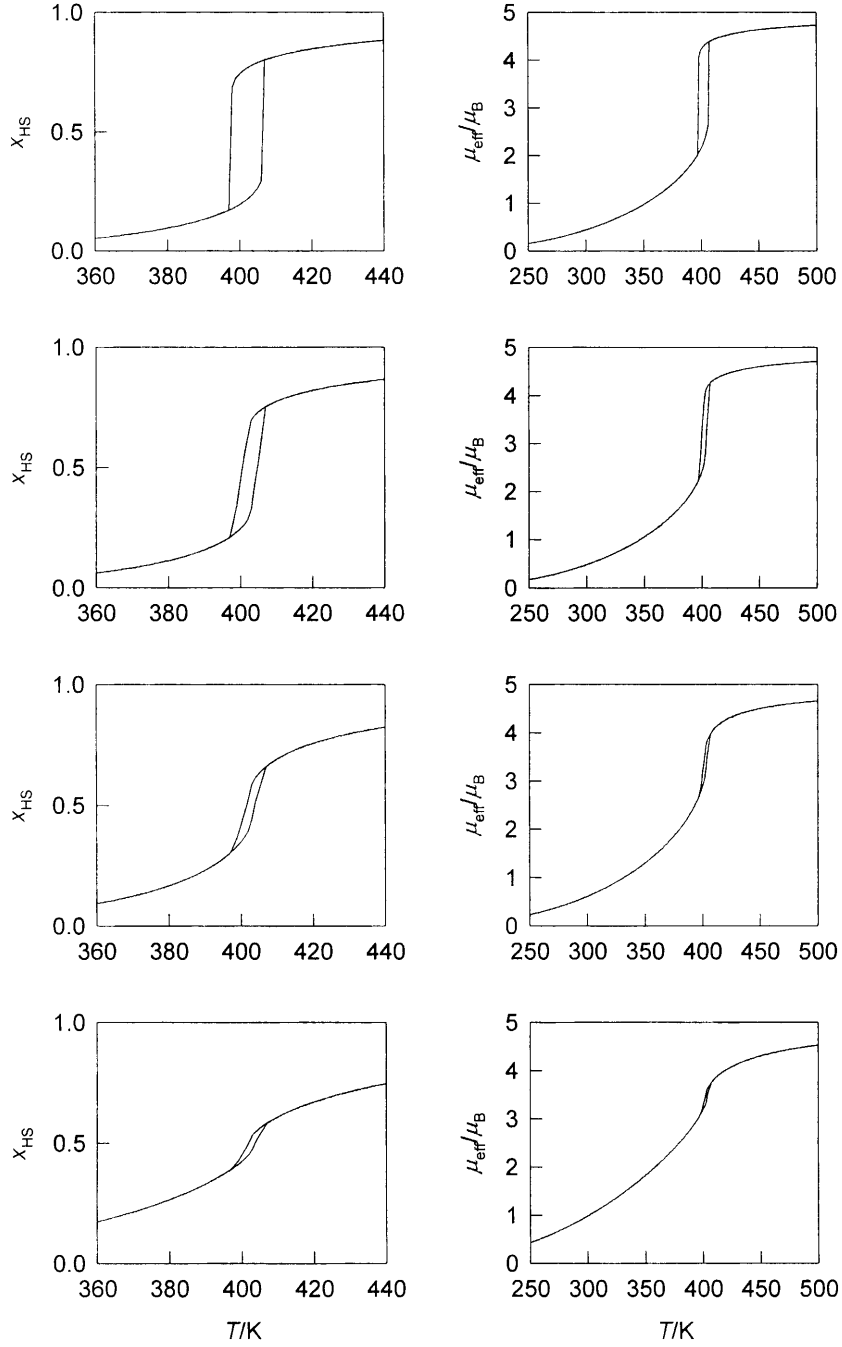


Fig. 5. Modeling of the spin crossover with a Gaussian distribution of the cooperativeness for $\delta = 0.00001, 0.01, 0.1, \text{ and } 1.0$. The other spin-crossover parameters were fixed ($\Delta_0/k = 2144 \text{ K}$, $J/k = 452 \text{ K}$, $r_{\text{eff}} = 205$; $g_{\text{HS}} = 2.0$); $0 \leq n_i \leq n_{\text{opt}} = n_{\text{max}} = 1$

$$E_{B2} = (\Delta_0/2) - (J_B \langle \sigma_B \rangle + J_{AB} \langle \sigma_A \rangle) \quad (56)$$

$$E_{B1} = -(\Delta_0/2) + (J_B \langle \sigma_B \rangle + J_{AB} \langle \sigma_A \rangle) \quad (57)$$

Thermal population within the *Boltzmann* statistics yields

$$\langle \sigma_A \rangle = \frac{-1 + K_A}{1 + K_A} \quad (58)$$

where

$$K_A = \frac{z_{A,HS}}{z_{A,LS}} = \frac{g_{HS}^{el} \exp(-E_{A2}/kT)}{g_{LS}^{el} \exp(-E_{A1}/kT)} = r_{eff} \exp[-(E_{A2} - E_{A1})/kT] \quad (59)$$

$$r_{eff} = g_{HS}^{el}/g_{LS}^{el} \quad (60)$$

and analogously for the sublattice B. Then two coupled equations should be fulfilled simultaneously

$$\langle \sigma_A \rangle = \frac{-1 + r_{eff} \exp\{-[\Delta_0 - 2(J_A \langle \sigma_A \rangle + J_{AB} \langle \sigma_B \rangle)]/kT\}}{1 + r_{eff} \exp\{-[\Delta_0 - 2(J_A \langle \sigma_A \rangle + J_{AB} \langle \sigma_B \rangle)]/kT\}} \quad (61)$$

$$\langle \sigma_B \rangle = \frac{-1 + r_{eff} \exp\{-[\Delta_0 - 2(J_B \langle \sigma_B \rangle + J_{AB} \langle \sigma_A \rangle)]/kT\}}{1 + r_{eff} \exp\{-[\Delta_0 - 2(J_B \langle \sigma_B \rangle + J_{AB} \langle \sigma_A \rangle)]/kT\}} \quad (62)$$

These equations can be solved by an iterative procedure. The free parameters of the model cover J_A , J_B , J_{AB} , Δ_0 , and r_{eff} . For modeling see Fig. 6.

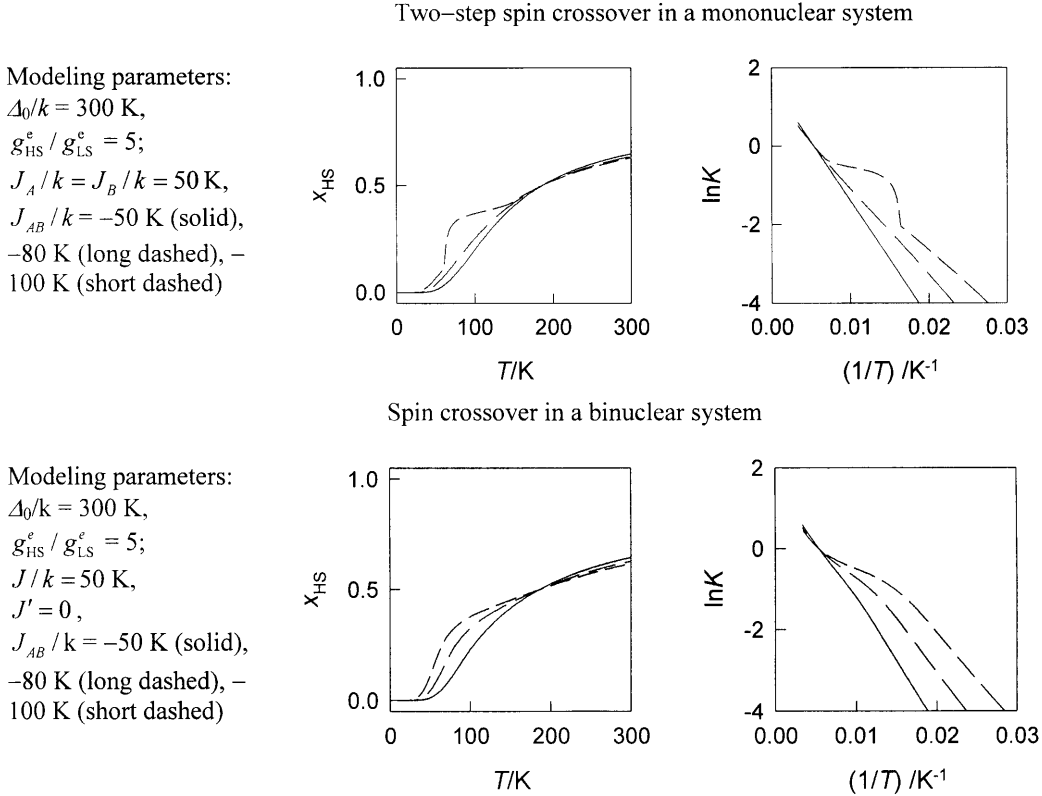


Fig. 6. Modelling of the spin crossover for a two-step case and a binuclear complex

Need of New Models?

Model for Binuclear Compounds

The case of the binuclear compounds formed of a symmetric pair of metallic centers the *Ising*-like Hamiltonian is

$$\hat{H} = -J_{AB}(\hat{\sigma}_A \cdot \hat{\sigma}_B) + \frac{\Delta_0}{2}(\hat{\sigma}_A + \hat{\sigma}_B) - J(\langle\sigma_A\rangle\hat{\sigma}_A + \langle\sigma_B\rangle\hat{\sigma}_B) - J'(\langle\sigma_A\rangle\hat{\sigma}_B + \langle\sigma_B\rangle\hat{\sigma}_A)$$

The intracomplex A–B interaction parameter J_{AB} adopts positive values for a “ferromagnetic-like” (cooperative) interaction of the fictitious spins. This has nothing to do with the isotropic exchange coupling constant J_{ex} that determines the energy levels in a binuclear system and has some connection to the site-formation energy. The intermolecular interaction parameters are J for A···A and B···B pairs, and J' for A···B and B···A, respectively (these are eventually neglected). The energy levels results in the form (see Fig. 7)

$$E_1(\sigma_A = -1, \sigma_B = -1) = E_{\text{LL}} = -\Delta_0 + (\langle\sigma_A\rangle + \langle\sigma_B\rangle)(J + J') - J_{AB} \quad (63)$$

$$E_2(\sigma_A = -1, \sigma_B = +1) = E_{\text{LH}} = (\langle\sigma_A\rangle - \langle\sigma_B\rangle)(J - J') + J_{AB} \quad (64)$$

$$E_3(\sigma_A = +1, \sigma_B = -1) = E_{\text{HL}} = -(\langle\sigma_A\rangle - \langle\sigma_B\rangle)(J - J') + J_{AB} \quad (65)$$

$$E_4(\sigma_A = +1, \sigma_B = +1) = E_{\text{HH}} = \Delta_0 - (\langle\sigma_A\rangle + \langle\sigma_B\rangle)(J + J') - J_{AB} \quad (66)$$

The partition function of the system is constructed as follows

$$Z = \sum_{i=1}^4 g_i \exp(-E_i/kT) \\ = g_{\text{LS}}^2 [\exp(-E_1/kT) + r_{\text{eff}} \exp(-E_2/kT) + r_{\text{eff}} \exp(-E_3/kT) + r_{\text{eff}}^2 \exp(-E_4/kT)]$$

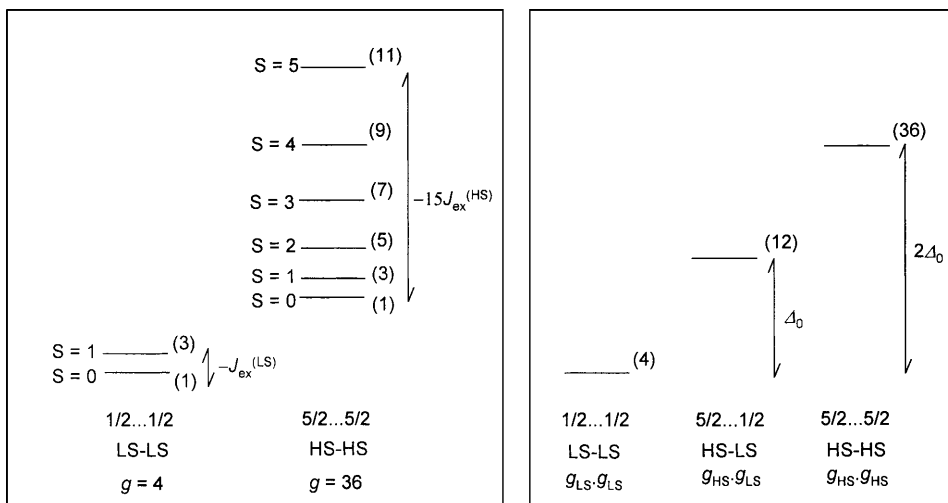


Fig. 7. A relationship between the energy levels of the isotropic (*Heisenberg*) exchange (left) and the *Ising*-like model of the spin crossover (right) for a binuclear Fe(III) complex. Degeneracies of the respective energy levels are given in parenthesis

where the effective degeneracy ratio, r_{eff} , occurs. The thermal average of the individual (formal) spin values are calculated as follows

$$\begin{aligned}\langle\sigma_A\rangle &= \sum_{i=1}^4 \sigma_{A,i} g_i \exp(-E_i/kT) \\ &= g_{\text{LS}}^2 [-\exp(-E_1/kT) - r_{\text{eff}} \exp(-E_2/kT) \\ &\quad + r_{\text{eff}} \exp(-E_3/kT) + r_{\text{eff}}^2 \exp(-E_4/kT)]/Z\end{aligned}\quad (67)$$

and

$$\begin{aligned}\langle\sigma_B\rangle &= g_{\text{LS}}^2 [-\exp(-E_1/kT) + r_{\text{eff}} \exp(-E_2/kT) - r_{\text{eff}} \exp(-E_3/kT) \\ &\quad + r_{\text{eff}}^2 \exp(-E_4/kT)]/Z\end{aligned}\quad (68)$$

Such a pair of the coupled equations can be solved by an iterative procedure. When $J=J'$ are assumed, the values of $\langle\sigma_A\rangle$ and $\langle\sigma_B\rangle$ are necessarily equal. Finally, the high-spin mole fraction is

$$x = (2 + \langle\sigma_A\rangle + \langle\sigma_B\rangle)/4\quad (69)$$

The modeling is shown in Fig. 6 and some recent applications were presented elsewhere [24].

Application of the Distribution Model

A need of the new spin crossover model has been motivated by some experimental facts that could not be explained by previous models. The molecular complex $[\text{Fe}(\text{bzimpy})_2](\text{ClO}_4)_2 \cdot 0.25\text{H}_2\text{O}$ (hereafter **1**) was identified as a spin crossover system with high transition temperature of $T_c = 403$ K and a hysteresis width of 12 K. This is true for a freshly prepared microcrystalline sample [20]. On the sample aging and its treatment like graining a marked loss of the cooperativeness is observed which manifests in these features of the conversion curve: 1) the hysteresis width becomes lower; 2) the wall of the hysteresis loop become more angled; 3) a back-ground signal increases; 4) the conversion seem be incomplete. The distribution model D is quite successful in reproducing of all these features, as shown in Fig. 8.

One could expect that the above model can be applied to some other cases. A loss of the cooperativeness has been identified for $[\text{Fe}(\text{PM-BiA})_2(\text{NCS})_2]$ when passing from the crystalline sample 1 to its powder counterpart 2 prepared by a fast precipitation [25]. The dilution of the $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ complex in an analogous Zn-matrix led to a systematic decrease of the abruptness (cooperativeness) of the conversion curves as well as a decrease of T_c that correlates with the dilution degree [26]. A decrease of the transition temperature along with a change of the profile of the conversion curve has been observed in $[\text{Fe}(\text{pap})_2]\text{ClO}_4$ system as a time effect [27]: one weak after preparation gave a substantial effect.

Remember that the cooperativeness has its origin in the intercentre interaction (irrespective of its nature). Thus any break of such an interaction (point defects, dislocations, surfaces, hetero-atoms, degradation and oxidation products) will lower cooperativeness in a statistical manner.

Need of New Models?

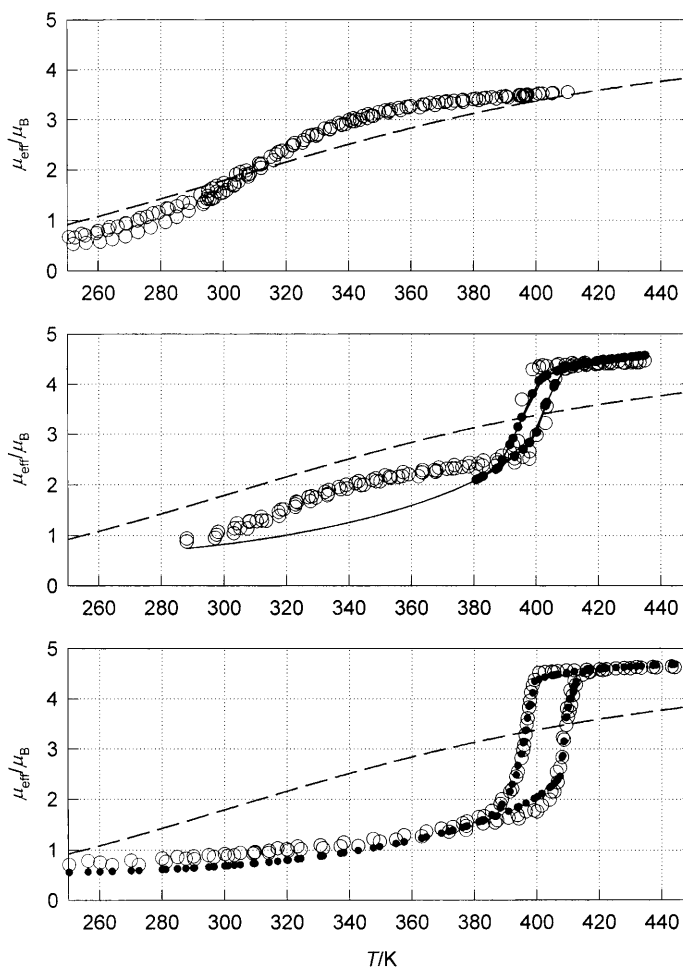


Fig. 8. Temperature variation of the effective magnetic moment (open symbols) for samples of **1** with different history (top – a one year-old sample, center – three-month old and powdered sample, bottom – a freshly prepared microcrystalline sample). Full points – fitted data using the theoretical model D. Solid line (center) – predicted. Dashed line – a theoretical curve in the absence of the cooperativeness

A Need of New Models

Not all experimental data were reproduced satisfactorily by the existing models of the spin crossover. The first problem occurs when the hysteresis loop possesses a strong asymmetry as found experimentally many times [30–33].

Second, a general, appropriate model should recover not only the conversion curve (usually constructed of the magnetic susceptibility data or the *Mössbauer* spectra data) but also the whole profile of the heat capacity [34].

Third, there are three-nuclear and polynuclear complexes exhibiting the spin crossover. A successful model for them is absent so far.

Fourth, a more complete inclusion of the interactions in the solid state is feasible, as outlined elsewhere [28, 35].

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