

## **Comparative analysis of the Ising-like Hamiltonian and molecular statistical models of spin crossover**

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Theoretical background and practical consequences of the use of the title models to parameterise equilibria between high-spin and low-spin isomers of transition metals complexes in the solid state are analysed. These models yield formally identical descriptions of *one-step* spin crossover systems, however, they assign different meaning to formal parameters. The fundamental difference of between the analysed models reveals itself in the description of *two-step* spin crossover systems. The molecular statistical model explicitly takes into account molecular interactions and ordering whereas the Ising-like Hamiltonian model considers HS-LS transitions of independent molecules occurring in interacting sublattices.

### **Introduction**

The phenomenon of spin crossover continues to attract the interest of scientists (see reviews <sup>1-10</sup>). Spin crossover presents a unique case of a solid-state homogeneous equilibrium between high-spin (HS) and low-spin (LS) isomers of coordination compounds of Fe(II) and several other ions. This equilibrium is accompanied by critical phenomena arising from molecular interactions (like abrupt spin crossover, two-step spin crossover, etc.).

A planned synthesis of spin-crossover compounds (having some potential for information storage and display devices) based theoretical predictions, requires a *molecular theory* of the phenomenon. Such

a theoretical model should explain the abruptness of transition, the transition temperature and the width of the hysteresis loop in terms of molecular parameters. It must provide adequate description of experimental data yielding well-defined estimates of physically meaningful parameters. Spin crossover occurs at low temperatures. Molecules in the spin equilibrium are quite similar, however, their diameters differ usually up to 10%. Sharp differences in magnetic and spectral properties of HS and LS isomers do not significantly affect molecular interactions. These specific features of spin-crossover systems facilitate the application of fundamental theoretical models.

On the one hand spin crossover is a chemical equilibrium and thus belongs to chemistry with its molecular-atomistic approach. On the other hand an important role in spin crossover play phase transitions that are traditionally the domain of physics with its continuum-field approach. This dualism of the phenomenon of spin crossover brings about a rich diversity of theoretical model employed to explain it.

It was quite natural that first models of spin crossover were related to the theory of magnetic phenomena. The model based on the Ising-like Hamiltonian (J. Wajnflasz, 1970<sup>11</sup>) was further developed in the works of R. Bari и J. Sivardiere (1972, <sup>12</sup>), V.V. Zelentsov *et al.* (1986<sup>13</sup>) and F. Varret *et al.* (1992<sup>14,15</sup>). It provides for an adequate formal description of all known types of spin crossover curves, both one-step and two-step. The *model of elastic interactions* considers species in equilibrium as incompressible spheres of different sizes immersed in an elastic medium <sup>17,18</sup>. This formalism is similar to that of the Ising-like Hamiltonian.

Thermodynamic models of spin crossover consider this phenomenon as a *chemical equilibrium in non-ideal systems*. The *model of regular solutions* <sup>16</sup> explains *the abrupt spin crossover* as a result of separation of HS-rich and LS-rich phases. Experimentally observed peaks of heat capacity <sup>9</sup> confirm the existence of such phase transitions. However this model (as well as the model of elastic interactions) does not predict two-step spin transitions. Some years ago we have proposed a *molecular statistical model* of spin crossover (MSM, <sup>19-25</sup>) that provided for adequate description of a wide variety of experimental transition curves, both one- and two-step. In the present paper we compare theoretical backgrounds and results of practical applications of this model and the model of the Ising-like Hamiltonian.

## One-step spin crossover

The Ising-like Hamiltonian model of spin crossover (IHM) employs the approximation of the mean-field. The Hamiltonian can be written (following F. Varret *et al.* <sup>14</sup>) as:

$$\mathcal{H} = \frac{\Delta_0}{2} \sigma - J \langle \sigma \rangle \sigma \quad (1)$$

in which  $\Delta_0$  is the energy difference between HS and LS states;  $J$  is the *interaction constant*,  $\sigma$  is the operator of the *fictitious spin* having eigenvalues  $\sigma = +1$  for HS and  $\sigma = -1$  for LS-states. For the sake of brevity we denote LS and HS molecules respectively as A and B isomers. The mean value of the operator  $\sigma$  reflects the difference of populations of HS and LS-states:

$$\langle \sigma \rangle = 2x_B - 1 = x_B - x_A \quad (2)$$

in which  $x_A$  and  $x_B$  are mole fractions of corresponding isomers. Positive constants  $J$  facilitate the formation of homo-molecular pairs (HS-HS and LS-LS), hence these interactions are called *ferromagnetic-like*. Reverse case of negative  $J$  (stabilisation of HS - LS pairs) is ascribed to *antiferromagnetic-like* interactions. This terminology is slightly confusing because *antiferromagnetic exchange* interactions in polynuclear spin-crossover compounds contribute to *ferromagnetic-like* interactions<sup>23</sup>.

The IHM model considers molecules as pseudo-independent molecules thus obeying the Maxwell-Boltzmann distribution. The mean value  $\sigma$  can then be computed as:

$$\langle \sigma \rangle = \frac{\sum_i \sigma_i g_i \exp(-E_i/kT)}{\sum_i g_i \exp(-E_i/kT)} \quad (3)$$

in which  $g_i$  is the degeneracy of the  $i$ -th state. The Hamiltonian (1) yields two eigenstates with energies  $E(-1) = -\frac{1}{2}\Delta_0 + J\langle\sigma\rangle$  and  $E(+1) = +\frac{1}{2}\Delta_0 - J\langle\sigma\rangle$ . Entering these energies into (3) results in:

$$\langle \sigma \rangle = \frac{-1 + \frac{g_B}{g_A} \exp\left(-\frac{\Delta_0 - 2J\langle\sigma\rangle}{kT}\right)}{1 + \frac{g_B}{g_A} \exp\left(-\frac{\Delta_0 - 2J\langle\sigma\rangle}{kT}\right)} \quad (4)$$

in which  $g_A$ ,  $g_B$  are degeneracies of LS and HS states respectively. From (4) one straightforwardly obtains:

$$\frac{x_B}{1-x_B} = \frac{g_B}{g_A} \exp\left(-\frac{\Delta_0 + 2J(1-2x_B)}{kT}\right) \quad (5)$$

For octahedral spin-crossover complexes of Fe(II) in HS state (term  ${}^5T_1$ ) spin degeneracy equals  $g_B = 5$ ; if we also take into account orbital degeneracy then  $g_B = 15$ . The ground state of octahedral Fe(II) complexes is  ${}^1A_1$  and  $g_A = 1$ .

Eq. (5) can be written in a more general form:

$$RT \ln \frac{x_B}{1-x_B} = -\Delta F^0 - 2J(1-2x_B) \quad (6)$$

in which  $\Delta F^0 = \Delta E^0 - T\Delta S^0$  is the standard Helmholtz free energy of spin crossover. Spin crossover significantly affects vibrational frequencies that contributes towards free energy:

$$\Delta F_{vib}^0 = -RT \sum \ln \frac{\sinh(\theta_A/2T)}{\sinh(\theta_B/2T)} \quad (7)$$

in which  $\theta_{A,B}$  are vibrational frequencies in K. Low-frequency vibrations ( $\theta \ll 2T$ , rotational oscillations and lattice vibrations) affected by spin crossover contribute solely towards the entropy of spin crossover. On the other hand, high-frequency vibrations ( $\theta \gg 2T$ , internal vibrations in ligands) contribute towards the energy of spin crossover. Stretching vibrations of the metal-to-ligand bonds, most affected by spin crossover, have frequencies in the region 300 - 600K. They contribute to both the energy and entropy of spin crossover. Vibrational contribution towards the free energy of spin crossover sometimes is considered in terms of the effective ratio of degeneracies ( $\Delta F_{vib}^0 = RT \ln(g_B/g_A)_{eff}$ ) that may reach  $(g_B/g_A)_{eff} = 500$ .<sup>15</sup>

Eq. (6) is formally identical to the corresponding equation of MSM in the approximation of binary interactions (Eq. (11)). Its properties will be considered below.

The molecular statistical model of spin crossover<sup>19-25</sup> considers the functional of the Helmholtz free energy of a binary mixture of pseudo-independent molecules. The probability to find a molecule of a given type in a lattice centre equals its mole fraction, mixing entropy is calculated according to the formulae of the ideal crystal and motions along axes are considered as uncorrelated. Molecular interactions are accounted for as the *effects of two nearest neighbours* on the partition function of the considered molecule<sup>19</sup>. The state of a molecule A in a mixture of isomers A (LS) and B (HS) can be characterised by the free energies  $F_{AAA}$ ,  $F_{BAA}$  and  $F_{BAB}$ . The same is valid for the central molecule B. Molecular interaction thus splits the free energy levels of molecules into triplets (Fig. 1).

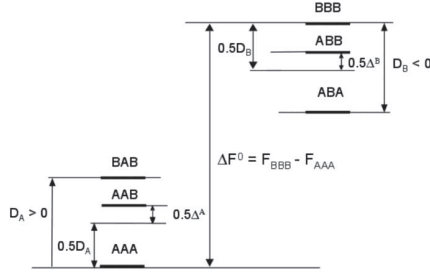


Fig. 1. The free energy levels diagram taking into account the effects of two nearest neighbours.

At a first glance such a model can only be valid for systems of weakly interacting 1D chains. However it has been shown<sup>25</sup> that the formalism of space lattices with negligibly weak or compensated many-body interactions of the order higher than 3 (ternary) is identical to the formalism derived for 1D chains.

Under the above-stated conditions the free energy of a mixture of A and B isomers has been obtained<sup>19,22</sup> as:

$$F = x_A x_B (x_A \Delta^A + x_B \Delta^B + D_A + D_B) + x_B \Delta F^0 + F_{AAA} + RT(x_A \ln x_A + x_B \ln x_B) \quad (8)$$

in which  $\Delta F^0 = F_{BBB} - F_{AAA}$  (Fig. 1). Main splitting  $D_A = F_{BAB} - F_{AAA}$  and  $D_B = F_{ABA} - F_{BBB}$  characterise the effects of a complete change of environment of a given molecule from homo- to hetero-molecular. Parameters  $\Delta^A = 2F_{AAB} - F_{AAA} - F_{BAB}$  and  $\Delta^B = 2F_{BBA} - F_{BBB} - F_{ABA}$  are the asymmetries of splittings characterising the efficiency of the first substitution in a homo-molecular environment. These splitting always appear as a sum that actually is the excess free energy:

$$\Delta F_{ex} = D_A + D_B = F_{BAB} - F_{AAA} + F_{ABA} - F_{BBB} \quad (9)$$

According to Eqs. (8, 9) the excess free energy reflects the *balance* of homo-and hetero-molecular *binary* interactions ( $x_A x_B \Delta F_{ex}$ ), whereas the asymmetries arise from ternary interactions:  $x_A x_B (x_A \Delta^A + x_B \Delta^B)$ . However deriving  $\Delta E_{ex}$ ,  $\Delta^A$  and  $\Delta^B$  from molecular potentials shows<sup>23</sup> that the excess free energy comprises contributions from both binary and ternary interactions whereas the asymmetries are completely controlled by ternary interactions. Entropic components of non-ideality parameters ( $\Delta F_{ex} = \Delta E_{ex} - T\Delta S_{ex}$ ,  $\Delta^{A(B)} = \Delta E^{A(B)} - T\Delta S^{A(B)}$ ) primarily arise from the changes of vibrational frequencies caused by the changes in molecular environment. These effects are usually small and  $\Delta F_{ex}$ ,  $\Delta^A$ ,  $\Delta^B$  can be considered as temperature independent energies.

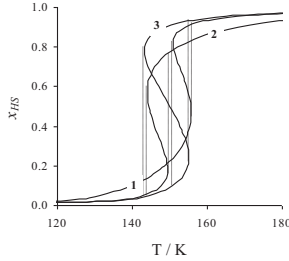
Taking into account (8) and  $x_A + x_B = 1$  the condition of the minimum of free energy with respect to composition,  $dF/dx_B = 0$ , can be written as <sup>22</sup>:

$$3(\Delta^A - \Delta^B)x_B^2 + 2(\Delta^B - 2\Delta^A - \Delta E_{ex})x_B + \Delta E_{ex} + \Delta^A + \Delta F^0 + RT \ln \frac{x_B}{1-x_B} = 0 \quad (10)$$

or:

$$T = \frac{3b_3x_B^2 + 2b_{20}x_B + b_1 + \Delta E^0}{\Delta S^0 - R \ln \frac{x_B}{1-x_B}} \quad (10a)$$

in which  $b_3 = \Delta^A - \Delta^B$ ;  $b_{20} = \Delta^B - 2\Delta^A - \Delta E_{ex}$ ;  $b_1 = \Delta E_{ex} + \Delta^A$  are coefficients introduced for brevity. If the medium-frequency vibrations ( $\theta \approx T$ ) are not significantly affected by spin transitions then  $\Delta S^0$  can be assumed to be temperature independent and transition curves may be computed straightforwardly from (10a) in the form  $T = f(x)$ . This approach is convenient to elucidate the physical nature of critical phenomena. For the regression purposes it is more convenient to use numerical solution of (10) and obtain transition curves in the form  $x_B = f(T)$ . This provides for simulation of curves with hysteresis and allows one to analyse the case of temperature dependent  $\Delta S^0$  (see e.g. in <sup>20</sup>).



**Fig. 2.** Spin crossover transition curves simulated according to (10a) for  $\Delta E^0 = 10$  kJ/mol,  $T_{1/2} = 150$  K,  $\Delta E_{ex} = 2.0$  kJ/mol and  $\Delta^A = 0$ ,  $\Delta^B = 1.5$  kJ/mol (2);  $\Delta^A = 1.5$  kJ/mol,  $\Delta^B = 0$  (3) and  $\Delta^A = \Delta^B = 1.5$  kJ/mol.

In the approximation of binary interactions ( $\Delta^A = \Delta^B = 0$ ) Eq. (10) becomes formally identical to Eq. (6) of the IHM:

$$-RT \ln \frac{x_B}{1-x_B} = \Delta E^0 - T\Delta S^0 + (1-2x_B)\Delta E_{ex} \quad (11)$$

in which the excess energy  $\Delta E_{ex}$  is an analogue of the interaction constant  $J = \frac{1}{2}\Delta E_{ex}$  (or the

cooperativity of the model of regular solutions<sup>16</sup>). Note that MSM interpret  $\Delta E_{ex}$  as reflecting the balance of homo- and hetero-molecular interactions (Eq. (9)) whereas IHM considers  $J$  as a formal parameter characterising the strength of interactions. Positive  $\Delta E_{ex}$  increases the slope of transition curves. At  $\Delta E_{ex} = 2RT_{1/2}$  ( $T_{1/2} = \Delta E^0/\Delta S^0$ ) the slope in the transition point ( $x_A = x_B = 1/2$ ) becomes infinite which corresponds to the case of the *abrupt spin crossover* without hysteresis. At larger positive  $\Delta E_{ex}$  the curves  $T = f(x_B)$  become S-shaped (similar to curve 3, Fig. 2). In the region of the loop several compositions correspond to the same temperature i.e. such systems are separated into HS- and LS-phases. States within the loop (according to negative values of  $d^2F/dx^2$ ) are unstable therefore spin crossover occurs as abrupt transitions showing hysteresis (dashed lines in Fig. 2).

When asymmetries are non-zero but equal  $\Delta^A = \Delta^B = \Delta \neq 0$  the coefficient  $b_j$  in (10a) is zero and the model is also reduced to the approximation of binary interactions (identical to IHM) with effective excess energy  $\Delta E_{ex} = D_A + D_B + \Delta$  (curve 3, Fig. 2). The MSM becomes different from IHM when  $\Delta^A \neq \Delta^B \neq 0$ . The non-zero quadratic term in (10) brings about asymmetry of transition curves (Fig. 2, curves 1 and 2), helpful when describing such experimental curves<sup>22</sup>. The tangent to the curve at  $x_B = 1/2$  is vertical when:

$$\frac{\Delta^B + \Delta^A}{2} + \Delta E_{ex} - \frac{R}{2\Delta S^0} (\Delta^B - \Delta^A) = 2RT_{1/2} \quad (12)$$

Positive asymmetries thus enhance the effect of positive  $\Delta E_{ex}$  whereas negative decrease it.

## Two-step spin crossover

According to MSM and IHM an abrupt spin crossover exhibiting a hysteresis is a result of separation of HS-rich and LS-rich phases in systems with homo-molecular interactions considerably stronger than hetero-molecular interactions. Formally these systems are characterised by positive excess energies. One should also expect some critical phenomena in systems characterised by large negative  $\Delta E_{ex}$ , i.e. when hetero-molecular pairs are significantly stronger than homo-molecular. However Eqs. (6), (9), (10) merely predict a monotonous decrease of the slope of transition curve with increasing negative  $J$ ,  $\Delta E_{ex}$ ,  $\Delta^A$ , or  $\Delta^B$ . This insensitivity towards hetero-molecular interactions originates from neglecting *ordering* phenomena.

In crystals, built of molecules of different types, interacting differently with each other, the total energy of molecular interactions depends not only on the composition, but also on the arrangement of molecules. There are several elegant theories of ordering that consider sublattices of  $\alpha$ - and  $\beta$ -centres in which  $\alpha$ -centres are surrounded by  $\beta$ -centres and *vice versa* (see e.g. in <sup>26</sup>). When sublattices are

filled in an ordered way (i.e. A in  $\alpha$ -centre and B in  $\beta$ -centre) the number of hetero-molecular contacts is maximal. At  $\Delta E_{ex} < 0$  the energy of molecular interactions of such ordered systems is minimal bringing about the formation of superstructures. Populations of sublattices by molecules of a given type can thus be used to quantify the phenomenon of ordering.

The molecular statistical model of spin crossover<sup>19</sup> employs the approximation of ordering developed by Gorsky, Bragg and Williams<sup>27,28</sup>. A basic simplification of this approximation corresponds to a non-selective filling of  $\alpha$  and  $\beta$  centres by A and B molecules. Ordering is characterised by a *degree of order*,  $s$ , defined *via* the probability of a molecule to get into a given centre. For  $x_B \leq 1/2$ , it is convenient to use  $s_B = 2p_B - 1$  in which  $p_B = N_B^\beta/N_B$  is the probability of a molecule B to get into a  $\beta$ -centre. According to MSM<sup>25</sup> the functional of free energy that takes into account ordering can be written as:

$$\begin{aligned}
 F(x_B, s_B) = & (1 - s_B^2) (\Delta^A - \Delta^B) x_B^3 \\
 & + \left[ (\Delta^B - 2\Delta^A - \Delta E_{ex}) + (\Delta E_{ex} - \Delta^B) s_B^2 \right] x_B^2 \\
 & + (\Delta E_{ex} + \Delta^A + \Delta F^0) x_B + F_{AAA} \\
 & + \frac{RT}{2} \ln \left[ u_{\beta\beta}^{u_{\beta\beta}} (1 - u_{\beta\beta})^{1 - u_{\beta\beta}} u_{\alpha B}^{u_{\alpha B}} (1 - u_{\alpha B})^{1 - u_{\alpha B}} \right]
 \end{aligned} \tag{13}$$

in which  $u_{\beta B} = (1 + s_B)x_B$ ,  $u_{\alpha B} = (1 - s_B)x_B$  are probabilities to find a  $\beta$ - (respectively  $\alpha$ -) centre occupied by a B-molecule. At  $x_B > 1/2$  and  $s_B \geq (1 - x_B)$  the argument of the logarithmic function in (13) becomes negative, hence the maximal value of  $s_B$  in this region must be:

$$s_B < (1 - x_B) / x_B < 1 \tag{14}$$

In order to avoid such an *a priori* condition (apparently neglecting superstructures formed by A-molecules) we have applied for the region  $x_B > 1/2$  the free energy functional  $F(x_A, s_A)$ , in which the degree of order  $s_A = 2p_A - 1$  is defined *via* the probability of a molecule A to get into an  $\alpha$ -centre,  $p_A = N_Y^\alpha / N_\alpha$ .

$$\begin{aligned}
 F(x_A, s_A) = & (1 - s_A^2) (\Delta^B - \Delta^A) x_A^3 \\
 & + \left[ \Delta^A - 2\Delta^B - \Delta F_{ex} + (\Delta F_{ex} - \Delta^A) s_A^2 \right] x_A^2 \\
 & + (\Delta F_{ex} + \Delta^B - F_{BBB} + F_{AAA}) x_A + F_{BBB} \\
 & + \frac{RT}{2} \ln \left[ u_{\alpha A}^{u_{\alpha A}} (1 - u_{\alpha A})^{1 - u_{\alpha A}} u_{\beta A}^{u_{\beta A}} (1 - u_{\beta A})^{1 - u_{\beta A}} \right]
 \end{aligned} \tag{15}$$

in which  $u_{\alpha A} = (1 + s)x_A$ ,  $u_{\beta A} = (1 - s)x_A$  are probabilities to find an  $\alpha$ - (respectively  $\beta$ -) centre occupied by an A-molecule and:



$$s_A < (1-x_A)/x_A < 1 \quad (16)$$

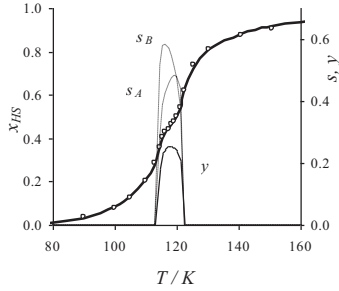
The functionals (13) and (15) yield different temperature dependencies of  $s_A$  and  $s_B$  (see Fig. 3), however, transition curves are identical. Therefore with limits set to the maximal value of the degree of order by (14), (16) any of these functionals can be used to describe transition curves in the whole region of compositions.

Ordering can be conveniently characterised by the *order parameter*  $y = x_A s_A = x_B s_B$  invariant with respect to the region of composition (see Fig. 3). On the other hand, the condition of the minimum of free energy should be formulated with respect to independent variables, such as  $x_A$ ,  $s_A$  or  $x_B$ ,  $s_B$ . whereas  $x_{A(B)}$  and  $y$  are not independent. Equilibrium then corresponds to zero coefficients at corresponding variations (e.g.  $(\partial F(x_B, s_B)/\partial x_B)_s = 0$ ;  $(\partial F(x_B, s_B)/\partial s_B)_x = 0$ ). Differentiating (13) one straightforwardly obtains:

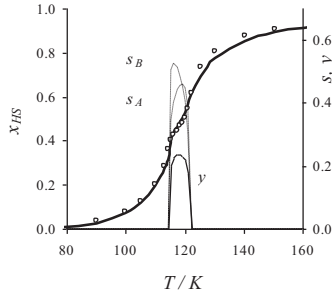
$$T = \frac{3(1-s_B^2)b_3x_B^2 + 2[b_{20} + s_B^2b_{22}]x_B + b_1 + \Delta E^0}{\Delta S^0 - \frac{R}{2} \ln \left( \frac{u_{\beta B}}{1-u_{\beta B}} \right)^{1+s_B} \left( \frac{u_{\alpha B}}{1-u_{\alpha B}} \right)^{1-s_B}} \quad (17)$$

$$T = \frac{4s_Bx_B(b_3x_B - b_{22})}{R \ln \frac{(1+s_B)(1-u_{\alpha B})}{(1-s_B)(1-u_{\beta B})}} \quad (18)$$

in which  $b_{22} = \Delta E_{ex} - \Delta^B$ . Solving (17, 18) numerically (see refs. <sup>19,20</sup>) simulates spin crossover transition curves. In the approximation of binary interactions ( $\Delta^A = \Delta^B = 0$ ) at large negative  $-\Delta E_{ex} > 2RT_{1/2}$  transition curves show a step connected with a peak of the degree of order <sup>19</sup>. However this approximation fails to describe quantitatively experimental data on the two-step spin crossover. An adequate description of experimental two-step transition curve of the 'prototypical' compound [Fe(2-pic)<sub>3</sub>]Cl<sub>2</sub>EtOH has been achieved<sup>19, 25</sup> in the approximation  $\Delta^A \neq \Delta^B \neq 0$  (Fig. 3A, first row in Table 1). The onset of ordering according to this model is spontaneous and abrupt in agreement with experimental XRD data<sup>30</sup>. The maximal value of  $s_B = 0.59$  (Table 1) obtained from the regression of transition curve differs from the XRD value ( $s_{max} = 0.72$ ) by less than 20%.



**Fig. 3A.** Parameterisation of the experimental transition curve of spin crossover in  $[\text{Fe}(2\text{-pic})_3]\text{Cl}_2\text{EtOH}$  (data from <sup>29</sup>) by MSM in the approximation of non-equal asymmetries. Estimates of parameters are shown in the first row of Table 1.



**Fig. 3B.** Parameterisation of the experimental transition curve of spin crossover in  $[\text{Fe}(2\text{-pic})_3]\text{Cl}_2\text{EtOH}$  <sup>29</sup> by MSM in the approximation of equal asymmetries. Estimates of parameters are shown in the second row of Table 1.

**Table 1.** Estimates of parameters of two models describing the two-step spin crossover in  $[\text{Fe}(2\text{-pic})_3]\text{Cl}_2\text{EtOH}$  <sup>29</sup>;  $\sigma_{yx}$  is the regression error,  $\Delta E^0$  was fixed according to calorimetric data <sup>9</sup>.

Model	$\sigma_{yx}$	$\Delta E^0$ kJ/mol	$T_{1/2}$ K	$\Delta S^0$ Дж/(мольК)	$\Delta^A(2J_\alpha)$ kJ/mol	$\Delta^B(2J_\beta)$ kJ/mol	$\Delta E_{cr}(2J_{int})$ kJ/mol	$s_{max}$ (exp. 0.72 [70])
MSM ( $\Delta^A \neq \Delta^B$ )	0.008	6.14	117.6±0.15	52.2±0.1	1.588±0.025	1.981±0.012	-0.379±0.008	0.59
MSM ( $\Delta^A = \Delta^B$ )	0.023	6.14	119.1±0.2	51.6±0.1	1.743±0.02	1.743±0.02	-0.398±0.023	0.52
IHM ( $J_\alpha = J_\beta$ )	0.023	6.14	119.1±0.2	51.6±0.1	1.754±0.003	1.754±0.003	-0.392±0.019	0.47
IHM ( $J_\alpha \neq J_\beta$ )	0.011	6.14	118.5±0.13	51.8±0.1	1.667±0.025	1.974±0.033	-0.367±0.008	0.50*

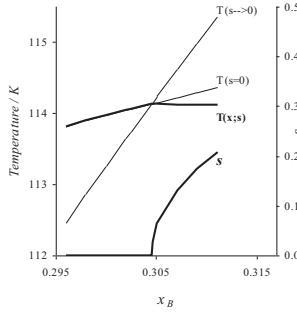
\*absolute value

Non-zero but equal asymmetries  $\Delta^A = \Delta^B \neq 0$  do not reduce this formalism to the approximation of binary interactions. This approximation provides for a convincing but not exactly adequate description of experimental data (Fig. 3B, second row of Table 1).

Critical temperatures and compositions corresponding to the onset of ordering ( $s \rightarrow 0$ ) can be found in the following way: Eq. (18) at  $s = 0$  yields uncertainty. Resolving it according to the L'Hospital rule one obtains the critical temperature of ordering for a mixture of a given composition:

$$T_{s \rightarrow 0} \approx \frac{2x_B(1-x_B)}{R}(b_3x_B - b_{22}) \quad (19)$$

On the other hand, approaching the critical point from disordered states the critical temperature can be computed at  $s = 0$  from (10a). At the border of the region of ordering these temperatures coincide  $T_{s \rightarrow 0} = T_{s=0}$  (Fig. 4), allowing one to find critical composition for given  $\Delta E^0$ ,  $\Delta S^0$ ,  $\Delta E_{ex}$ ,  $\Delta^A$ ,  $\Delta^B$  by solving (20) numerically.



**Fig. 4.** The behaviour of temperature dependencies of composition and degree of order at one of the borders of ordering computed for  $\Delta E^0 = 6.14$  kJ/mol,  $T_{1/2} = 117.6$  K,  $\Delta E_{ex} = -0.379$  kJ/mol;  $\Delta^A = 1.588$  kJ/mol;  $\Delta^B = 1.981$  kJ/mol (see. Table. 1).

$$T_{s_B=0} - T_{s_B \rightarrow 0} = \frac{3b_3x_B^2 + 2b_{20}x_B + b_1 + \Delta E^0}{\Delta S^0 - R \ln \frac{x_B}{1-x_B}} - \frac{2x_B(1-x_B)(b_3x_B - b_{22})}{R} = 0 \quad (20)$$

After finding the critical composition ( $x_B$ ) the critical temperature is straightforwardly computed from any of two ratios in (20). Theoretical transition curves computed according to (17, 18) lead to a discontinuity in the derivative  $dx_B/dT$  corresponding to points of the onset of ordering (Fig. 4, curve  $T(x,s)$ ). These discontinuities reflect transitions from the trivial to non-trivial solutions.

The model of the Ising-like Hamiltonian <sup>14,15</sup> also employs  $\alpha$  and  $\beta$  sublattices for the explanation of the two-step spin crossover. However, these sublattices play completely different roles compared to those in MSM. In the mean field approximation the total Hamiltonian is substituted by two one-centre Hamiltonians:

$$\mathcal{H}_\alpha = \frac{\Delta_0}{2} \sigma - (J_\alpha \langle \sigma_\alpha \rangle + J_{\alpha\beta} \langle \sigma_\beta \rangle) \sigma \quad (21)$$

$$\mathcal{H}_\beta = \frac{\Delta_0}{2} \sigma - (J_\beta \langle \sigma_\beta \rangle + J_{\alpha\beta} \langle \sigma_\alpha \rangle) \sigma \quad (22)$$

in which  $J_\alpha$ ,  $J_\beta$  and  $J_{\alpha\beta}$  characterise intra- and inter-sublattice interactions. Mean values of fictitious spins characterise the populations of these sublattices by HS molecules:

$$\langle \sigma_\alpha \rangle = 2 \frac{N_B^\alpha}{\frac{1}{2}N} - 1 \quad (23)$$

$$\langle \sigma_\beta \rangle = 2 \frac{N_B^\beta}{\frac{1}{2}N} - 1 \quad (24)$$

From (23, 24) the relationship between the mean values of fictitious spins and variables of MSM can be derived as:

$$x_A = \frac{2 - \langle \sigma_\alpha \rangle - \langle \sigma_\beta \rangle}{4}; \quad x_B = \frac{2 + \langle \sigma_\alpha \rangle + \langle \sigma_\beta \rangle}{4} \quad (25)$$

$$s_A = \frac{\langle \sigma_\beta \rangle - \langle \sigma_\alpha \rangle}{2 - \langle \sigma_\beta \rangle - \langle \sigma_\alpha \rangle}; \quad s_B = \frac{\langle \sigma_\beta \rangle - \langle \sigma_\alpha \rangle}{2 + \langle \sigma_\alpha \rangle + \langle \sigma_\beta \rangle} \quad (26)$$

$$y = s_A x_A = s_B x_B = \frac{\langle \sigma_\beta \rangle - \langle \sigma_\alpha \rangle}{4} \quad (27)$$

From eigenvalues of (21, 22) one obtains<sup>14</sup>:

$$\langle \sigma_\alpha \rangle = \frac{-1 + \frac{g_B}{g_A} \exp \left[ -\frac{\Delta_0 - 2J_\alpha \langle \sigma_\alpha \rangle - 2J_{\alpha\beta} \langle \sigma_\beta \rangle}{kT} \right]}{1 + \frac{g_B}{g_A} \exp \left[ -\frac{\Delta_0 - 2J_\alpha \langle \sigma_\alpha \rangle - 2J_{\alpha\beta} \langle \sigma_\beta \rangle}{kT} \right]} \quad (28)$$

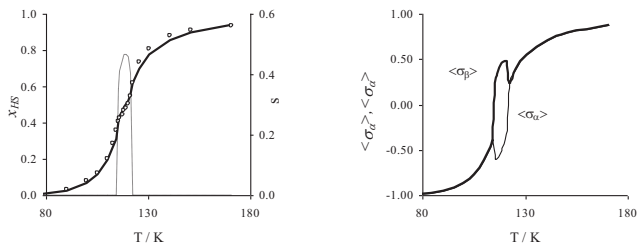
$$\langle \sigma_\beta \rangle = \frac{-1 + \frac{g_B}{g_A} \exp \left[ -\frac{\Delta_0 - 2J_\beta \langle \sigma_\beta \rangle - 2J_{\alpha\beta} \langle \sigma_\alpha \rangle}{kT} \right]}{1 + \frac{g_B}{g_A} \exp \left[ -\frac{\Delta_0 - 2J_\beta \langle \sigma_\beta \rangle - 2J_{\alpha\beta} \langle \sigma_\alpha \rangle}{kT} \right]} \quad (29)$$

Solutions of (28, 29) corresponding to non-ordered systems ( $s = 0$ ,  $\langle \sigma_\alpha \rangle = \langle \sigma_\beta \rangle$ ) are only possible when  $J_\alpha = J_\beta = J$ , *i.e.* in the approximations of *equivalent sublattices*. This approximation yields transition curves that show a step and a spontaneous onset of ordering ( $\langle \sigma_\alpha \rangle \neq \langle \sigma_\beta \rangle$ , “sublattice symmetry breaking”<sup>14</sup>) for large negative  $J_{\alpha\beta}$  and positive  $J$ , satisfying the condition  $J - J_{\alpha\beta} > RT_{1/2}$ .

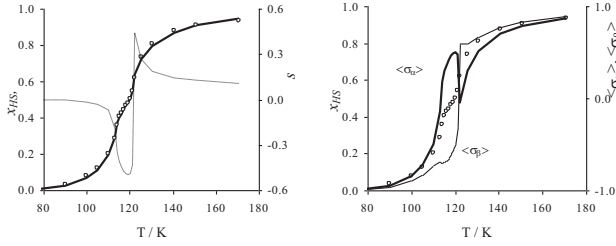
Outside the region of ordering the degree of order derived from (26) is exactly zero. The approximation  $J_\alpha = J_\beta = J$  provides for a qualitatively correct but not adequate description of experimental data on spin crossover in  $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2\text{EtOH}$ <sup>29</sup> (third row in Table 1, Fig. 5). This description is similar to that of MSM in the approximation of  $\Delta^A = \Delta^B$ ; they coincide quantitatively when  $s = 0$ , but in the region of ordering there is a difference in solutions of (17, 18) and (28, 29) above possible errors.

An adequate description of experimental data by IHM can be achieved in the approximation of *non-equivalent sublattices* ( $J_\alpha \neq J_\beta$ ). The accuracy of this description is comparable to that of MSM (Fig. 6, 4th row of Table 1). Estimates of parameters are very close to those obtained by regression according to MSM ( $\Delta E_{ex} \approx 2J_{\alpha\beta}$ ,  $\Delta^A \approx 2J_\alpha$ ,  $\Delta^B \approx 2J_\beta$ , compare 1st and 3d rows in Table 1). This striking coincidence was considered as an indication of formal equivalence of IHM and MSM. On the other hand, computations according to (17, 18) and (28, 29) employing  $J_{\alpha\beta} = \frac{1}{2}\Delta E_{ex}$ ;  $J_\alpha = \frac{1}{2}\Delta^A$ ;  $J_\beta = \frac{1}{2}\Delta^B$ , show that there is no exact equality of these models: transition curves differ significantly especially at the border of the region of ordering (by *ca.*  $\Delta x_B = 0.1$ , Fig. 7).

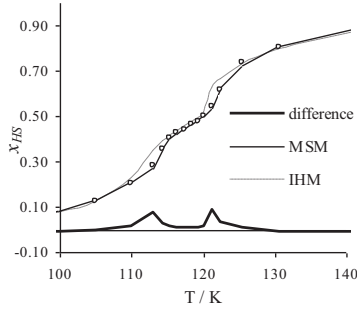
The above coincidence is apparently fortuitous, because the compared parameters refer to essentially different features:  $J_\alpha$ ,  $J_\beta$  and  $J_{\alpha\beta}$  refer to the properties of sublattices whereas  $\Delta^A$ ,  $\Delta^B$  and  $\Delta E_{ex}$  refer to molecular interactions. By ascribing different values to  $J_\alpha$  and  $J_\beta$  we introduce selectivity of  $\alpha$ - and  $\beta$ - centres towards molecules A and B. Therefore in the approximation of non-equivalent sublattices the IHM populations of  $\alpha$  and  $\beta$ -sublattices become unequal at any temperature. There is no *spontaneous* ordering (or ‘symmetry breaking’) and the degree of order remains non-zero in the whole range of compositions. Spontaneous ordering (supported by experimental XRD data<sup>30</sup>) is predicted by IHM in the approximation of equivalent sublattices ( $J_\alpha = J_\beta$ ) however this approximation fails to adequately parameterise the two-step transition curves.



**Fig. 5.** Approximation of experimental data on spin crossover in  $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2\text{EtOH}$ <sup>29</sup> by IHM with equivalent sublattices ( $J_\alpha = J_\beta$ ). Dashed line is the degree of order. Estimates of parameters are in the second row of Table 1. The right-hand graph shows variations of the mean values of fictitious spins



**Fig. 6.** Approximation of experimental data on spin crossover in  $[\text{Fe}(2\text{-pic})_3]\text{Cl}_2\text{EtOH}$  <sup>29</sup> by IHM with non-equivalent sublattices ( $J_\alpha \neq J_\beta$ ). Dashed line is the degree of order. Estimates of parameters are in the 3d row of Table 1. The right-hand graph shows variations of the mean values of fictitious spins



**Fig. 7.** Curves generated by IHM and MSM and their difference computed for fixed parameters ( $J_{\alpha\beta} = \frac{1}{2}\Delta E_{\text{ext}}$ ;  $J_\alpha = \frac{1}{2}\Delta^A$ ;  $J_\beta = \frac{1}{2}\Delta^B$ ) shown in the first row of Table 1.

In MSM the sublattices are always equivalent and the condition  $\Delta^A \neq \Delta^B$  means a non-zero contribution of ternary interactions, i.e. it is of a completely different nature than the condition  $J_\alpha \neq J_\beta$ . In fact the asymmetries  $\Delta^A$  and  $\Delta^B$  have been at first derived for non-ordered systems (Eq. (8), Fig. 1). MSM has thus an advantage of taking into account the phenomenon of ordering along with the binary and many-body interactions. Quantitative parameterisation of experimental data by the approximation of non-equivalent sublattices of IHM seems to be achieved in an artificial way. Mean values of fictitious spins  $\langle\sigma_\alpha\rangle$  and  $\langle\sigma_\beta\rangle$  synchronously change their signs (Fig. 6, right-hand graph). The accuracy of description is thus improved by an arbitrary change of selection rules during regression. The difference between IHM and MSM can be demonstrated analytically. Let us explicitly define temperature from (29, 30) as it has been done when deriving Eqs. (17, 18). Expressing then  $\langle\sigma_\alpha\rangle$  and  $\langle\sigma_\beta\rangle$  via  $x_B$  and  $s_B$  according to (25, 26) one obtains:

$$T = \frac{\Delta_0 + 2 \left[ J_\alpha + J_{\alpha\beta} - 2 \left( J_\alpha + J_{\alpha\beta} + (J_\alpha - J_{\alpha\beta}) s_B \right) x_B \right]}{\Delta S^0 - R \ln \frac{(1-s_B)x_B}{1-(1-s_B)x_B}} \quad (30)$$

$$T = \frac{\Delta_0 + 2 \left[ J_\beta + J_{\alpha\beta} - 2 \left( J_\beta + J_{\alpha\beta} - (J_{\alpha\beta} - J_\beta) s_B \right) x_B \right]}{\Delta S^0 - R \ln \frac{(1+s_B)x_B}{1-(1+s_B)x_B}} \quad (31)$$

in which  $\Delta S^0 = R \ln(g_B/g_A)$ . These equations drastically differ from corresponding equations of the MSM (17, 18): Equations (30) and (31) are symmetric, whereas Eqs. (17) and (18) obviously are of a different nature. The numerator of (30) contains  $s$  to the first power whereas in (17) it appears as  $s^2$ . Entropic terms in denominators of (30, 31) and (17, 18) are also fundamentally different at  $s \neq 0$ .

This dissimilarity originates from the fact that MSM considers the effects of molecular interactions on two distinct processes: chemical equilibrium (Eq. (17)) and ordering (Eq. (18)). IHM considers one process of transitions between HS and LS states in two sublattices, hence the symmetry of Eqs. (30) and (31). Sublattices in IHM implicitly represent molecular interactions, in a way similar to the elastic continuum of the model of elastic interactions. Compared to the latter model IHM has an advantage of introducing several such continua with different properties, providing thus for the description of the two-step spin crossover. Sublattices in MSM play a technical role of labelling “odd” and “even” centres. They are non-selective irrespective the values of non-ideality parameters ( $\Delta E_{ex}$ ,  $\Delta^A$ ,  $\Delta^B$ ) because the latter refer to molecular interactions and not to sublattices.

Estimates of  $J_\alpha$ ,  $J_\beta$  and  $J_{\alpha\beta}$  obtained from the transition curve of  $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2\text{EtOH}$  are difficult to explain from the point of view of molecular interactions. The inter-sublattice constant corresponds to the nearest neighbour interactions whereas intra-sublattice constants correspond to the next-to-nearest neighbour interactions. However this does not agree with the estimates:  $|J_{\alpha\beta}| \ll J_\alpha, J_\beta$ ;  $J_{\alpha\beta} < 0$ ;  $J_\alpha, J_\beta > 0$  (Table 1). Interactions constants thus are formal parameters reflecting the properties of sublattices rather than molecules. Estimates of parameters of MSM have been successfully interpreted in terms of molecular potentials. Representing ternary potentials ( $\psi$ ) as perturbations of binary potentials ( $\phi$ ) by external molecules ( $\psi_{ijk} = \alpha^k \phi_{ij}$ ) it has been shown<sup>25</sup> that, for spin crossover in the diamond lattice the non-ideality parameters of MSM can be written as:

$$\Delta E_{ex} = 4\Delta\phi_{ex} + 12\alpha\Delta\phi^0 \quad (32)$$

$$\Delta^A = -24\alpha(\phi_{AA} - \phi_{AB}) \quad (33)$$

$$\Delta^B = -24\alpha(\phi_{AB} - \phi_{BB}) \quad (34)$$

in which  $\Delta\varphi_{\text{ex}} = 2\varphi_{\text{AB}} - \varphi_{\text{AA}} - \varphi_{\text{BB}}$  is the interchange energy,  $\Delta\varphi^0 = \varphi_{\text{BB}} - \varphi_{\text{AA}}$ . Estimates of  $\Delta E_{\text{ex}}$ ,  $\Delta^{\text{A}}$  and  $\Delta^{\text{B}}$  can thus be used to calculate molecular parameters:  $\Delta\varphi_{\text{ex}}$ ,  $\Delta\varphi^0$  and  $\alpha$ . Values shown in the first row of Table 1 correspond to  $\Delta\varphi_{\text{ex}} = -0.541$  kJ/mol,  $\Delta\varphi^0 = +4.91$  kJ/mol and  $\alpha = 0.03$  which is in agreement with established views on the relative role of binary and many-body molecular interactions. Although a single effect of third body is quite insignificant these effects are numerous (see tables in <sup>25</sup>) and considerably affect the shape of spin crossover transition curves.

## Conclusions

Due to unique features of spin crossover: low temperatures of transitions and relatively small differences in molecular interactions of HS- and LS-isomers, quite simple fundamental models adequately describe very complicated experimental transition curves. Spin crossover is thus a perfect test-system for theoretical models of reactions in the condensed state. Two compared models are formally equivalent in the description of the one-step spin crossover. However the interpretation of parameters of these models is different. According to IHM the abrupt spin crossover originates from large positive interaction constants, hence from the ‘most intimate’ interaction of neighbouring complexes. According to MSM large positive excess energies required for sharp transitions arise from large *differences* of interaction energies in AA, BB and BB pairs <sup>23</sup>. It also puts certain accent on the role of many-centre interactions <sup>24, 25</sup>.

At a first glance, in order to explain hysteresis both formalisms exploit the incorrect prediction of the mean field approximation concerning the phase transitions in 1D systems not present in the exact solution of the Ising model <sup>31</sup>. Phase transitions predicted by IHM apparently are due to the long-range interactions implicitly contained in the mean-field approach<sup>31</sup>. By introducing ‘lattice’ properties, such as interaction constants, this model implicitly assumes the existence of macroscopically long-range forces. In fact the model of elastic interactions based on the assumption of infinite-range molecular forces employs the formalism identical to that of the Ising-like Hamiltonian<sup>32</sup>.

MSM does not employ any sublattice properties. Its parameters arise from binary and many-body interactions between molecules. Phase transitions predicted by MSM for 1D chains should be ascribed to those in 3D or 2D structures with weak or compensated many-body interactions of the order above ternary<sup>25</sup>. Compared models fundamentally differ in the description of the two-step spin crossover, namely in accounting for the phenomenon of ordering. Two-step transition curves simulated by IHM and MSM are similar but not identical. Equations of IHM and ISM being transformed to a comparable form are distinctly different. MSM explicitly considers the effects of



molecular interactions on *two processes*: chemical equilibrium and ordering. Oppositely, IHM considers one process of transitions between independent HS- and LS-states in the interacting sublattices.

The original model of Ising was developed for the description of systems in which transitions between “spin-up” and “spin-down” states do not change the chemical nature of the involved centres, however, the interaction energy strongly depends on the states of interacting particles. The chemical nature of HS- and LS-isomers is different due to *ca.* two times stronger ligand field of the LS-state, whereas the energy of molecular interactions is not particularly sensitive to the spin-state. Magnetic exchange interaction energy is only a small part of the total energy of molecular interaction in spin crossover systems<sup>23</sup>. MSM has been derived as to meet these requirements, whereas IHM adjusts the formalism derived for distinct systems.

The advantage of IHM lies in the simplicity of the mathematical formulae providing at the same time for adequate formal description of the majority of experimental data on spin crossover. MSM employs a slightly more complicated formalism with the same number of parameters. It yields adequate description of a wide variety of transition curves<sup>20,22</sup> with well-defined estimates of parameters that can be rationally interpreted in terms of molecular potentials. The order of magnitude of estimates of the MSM parameters agrees with the established views on the role of binary and ternary molecular interactions. MSM thus provides for a better understanding of the molecular nature of cooperative phenomena observed in spin crossover, which is important for defining the strategy of the synthesis of promising compounds.

## Methods

Experimental data have been extracted from a graph in the quoted article<sup>29</sup>. Details on the computational realisation of MSM and non-linear regression can be found in refs. <sup>19,20,33</sup>. The system of equations (29, 30) has been solved numerically using the Newton-Gauss method. This procedure has been incorporated into a non-linear regression program as described in ref. <sup>33</sup>.

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