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ORIGINAL PAPER

Free energy functional of the Ising-like model of spin crossover

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Abstract The model of spin crossover based on the Ising-like Hamiltonian (IHM) has been analysed by deriving the functional of free energy from the mean-field solutions of this Hamiltonian. The contribution of the configurational entropy was found to be identical to that in the functional of the molecular statistical model (MSM) of spin crossover. However, the polynomial expansion over composition (x_B) and degree of order (s_B) in these functionals differ fundamentally due to different ways of accounting for the effects of molecular interactions. It was found that IHM takes into account next-to-nearest neighbour interactions by introducing affinities of sublattices towards molecules of given kinds. This yields a term proportional to the first power of the degree of order in the functional of IHM, whereas the MSM free energy is only proportional to s_B^2. The choice of formal independent variables does not affect the results of simulations of transition curves provided the functional remains unaltered. This provides for more flexibility in numerical simulations of transition curves.

Keywords Spin crossover · Ising-like Hamiltonian · Free energy functional

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Introduction

The equilibrium between high-spin (HS) and low-spin (LS) isomers of some transition metal complexes [1–4] known as spin crossover presents an example of a homogeneous chemical equilibrium in the solid state. Being of practical interest for building spintronic devices [5–7], it is also useful as a test system for various theories of chemical reactions in the solid state. Although spin crossover shows certain features arising from strong molecular interactions (abrupt transitions with hysteresis, two-step spin crossover) it can be quantitatively parameterised by employing simple theoretical models [4, 8, 9].

The most widely used Ising-like Hamiltonian model (IHM [10–13]) yields adequate description of the majority of typical transition curves of spin crossover. Parameters of this model, although being in principle formal, are interpreted as reflecting the strength of molecular interactions [14].

An alternative approach to the description of spin crossover has been developed within the molecular statistical model (MSM [15–17]) based on the functional of free energy derived for a system of binary and many-body molecular interactions. This model not only adequately describes quite complicated transition curves but also gives insight into the molecular nature of interaction parameters. This is very important when establishing a strategy of synthesis of promising spin-crossover compounds exhibiting high cooperativity.

Comparative analysis of IHM and MSM has shown that they are formally identical in the description of the one-step spin crossover; however, these models differently approximate two-step transition curves [4, 18].

In the present paper, we shall derive and analyse the functional of free energy of the IHM and consider fundamental implications of IHM and MSM approaches.

Results and discussion

One-sublattice model

Let us consider the energy level pattern of the simplest model of spin crossover, viz. Ising-like Hamiltonian in the mean-field approximation [13]:

$$H = \frac{\Delta E^0}{2}\boldsymbol{\sigma} - J\langle\sigma\rangle\boldsymbol{\sigma} \tag{1}$$

where $\boldsymbol{\sigma}$ is the operator of the fictitious spin having eigenvalues $\sigma = +1$ (HS) and $\sigma = -1$ (LS), ΔE^0 is the energy splitting between isolated HS and LS states, J is the interaction constant and $\langle\sigma\rangle$ is the mean value of fictitious spin that reflects the population of the lattice by HS states.

$$\langle\sigma\rangle = 2\frac{N_{\text{HS}}}{N} - 1 = 2x_{\text{HS}} - 1 = x_{\text{HS}} - x_{\text{LS}} \tag{2}$$

in which x_{LS}, x_{HS} are mole fractions of LS and HS states. For brevity, we shall further refer to the LS state as A, and to HS state as B. According to Eq. 1, the energy of a molecule in a lattice centre depends, first of all, on the state in which it exists ($+\Delta E^0/2$ for B and $-\Delta E^0/2$ for A) and, secondly, on the composition of the lattice (that may be interpreted as the nearest surroundings) defined by the mean value of the fictitious spin (Fig. 1).

The Hamiltonian (Eq. 1) has been written in such a way that at positive J the molecules in homo-molecular surroundings (A surrounded by A and B surrounded by B) are more stable. This case is referred to as the ferromagnetic-like interaction. Inversely, when the interaction constant is negative molecules in heteromolecular surroundings become more stable realising thus the case of the antiferromagnetic-like interaction.

Supposing molecules to be independent one can apply the Maxwell–Boltzmann statistics and compute the mean value of the fictitious spin as:

$$\langle\sigma\rangle = \frac{\sigma_{\text{A}} g_{\text{A}} \exp(-E_{\text{A}}/kT) + \sigma_{\text{B}} g_{\text{B}} \exp(-E_{\text{B}}/RT)}{g_{\text{A}} \exp(-E_{\text{A}}/kT) + g_{\text{B}} \exp(-E_{\text{B}}/RT)} = \frac{-1 + \frac{g_{\text{B}}}{g_{\text{A}}}\exp\left(-\frac{E_{\text{B}}-E_{\text{A}}}{RT}\right)}{1 + \frac{g_{\text{B}}}{g_{\text{A}}}\exp\left(-\frac{E_{\text{B}}-E_{\text{A}}}{RT}\right)} \tag{3}$$

in which g_{A}, g_{B} are the degeneracies of the corresponding states. Entering eigenvalues of Eq. 1:

$$E_{\text{A}} = -\frac{\Delta E^0}{2} + J\langle\sigma\rangle; \quad E_{\text{B}} = +\frac{\Delta E^0}{2} - J\langle\sigma\rangle; \tag{4}$$

into Eq. 3 one obtains:

$$\langle\sigma\rangle = \frac{-1 + \frac{g_{\text{B}}}{g_{\text{A}}}\exp\left(-\frac{\Delta E^0 - 2J\langle\sigma\rangle}{RT}\right)}{1 + \frac{g_{\text{B}}}{g_{\text{A}}}\exp\left(-\frac{\Delta E^0 - 2J\langle\sigma\rangle}{RT}\right)} \tag{5}$$

or:

$$\ln\frac{\langle\sigma\rangle + 1}{1 - \langle\sigma\rangle} - \ln\frac{g_{\text{B}}}{g_{\text{A}}} + \frac{\Delta E^0 - 2J\langle\sigma\rangle}{RT} = 0 \tag{5a}$$

or:

$$\ln\frac{x_{\text{B}}}{1 - x_{\text{B}}} - \ln\frac{g_{\text{B}}}{g_{\text{A}}} + \frac{\Delta E^0 - 2J(2x_{\text{B}} - 1)}{RT} = 0 \tag{5b}$$

Experimental studies of spin crossover have shown that purely spin degeneracies or spin and orbital degeneracies ($g_{\text{Bspin}} = 5$ and $g_{\text{Bspin}}g_{\text{Borb}} = 15$ for Fe(II) complexes) cannot explain large estimates of $\ln(g_{\text{B}}/g_{\text{A}}) = 4$–$12$. Therefore, the term $R\ln(g_{\text{B}}/g_{\text{A}})$ is considered as the entropy of spin crossover comprising electronic and vibrational contributions [4].

The functional of free energy of the model based on the Hamiltonian defined in Eq. 1 can be derived by considering Eq. 5a as the condition of the minimum of free energy with respect to the mean value of fictitious spin:

$$\left(\frac{\partial F}{\partial\langle\sigma\rangle}\right)_T = RT[\ln(\langle\sigma\rangle + 1) - \ln(1 - \langle\sigma\rangle)] + \Delta E^0 - T\Delta S^0 - 2J\langle\sigma\rangle = 0 \tag{6}$$

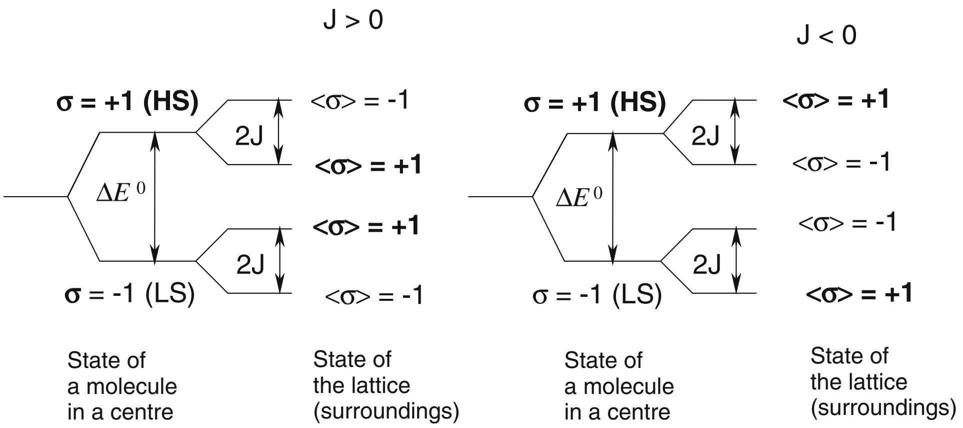

Fig. 1 Energy level diagrams of a molecule in a lattice centre drawn for the IHM model

Integrating this equation along $\langle\sigma\rangle$ one obtains:

$$\begin{aligned} F = RT[(\langle\sigma\rangle + 1)\ln(\langle\sigma\rangle + 1) + (1 - \langle\sigma\rangle)\ln(1 - \langle\sigma\rangle) - 2] \\ + \left(\Delta E^0 - T\Delta S^0\right)\langle\sigma\rangle - J\langle\sigma\rangle^2 + \varphi(T) \end{aligned} \tag{7}$$

where $\varphi(T)$ is an unknown function of temperature that appears because the condition of the minimum was written via a partial derivative. Substituting in Eq. 7 fictitious spin by the composition one obtains:

$$\begin{aligned} \frac{1}{2}F = RT[x_B\ln(x_B) + (1 - x_B)\ln(1 - x_B)] \\ + \left(\Delta E^0 - T\Delta S^0\right)x_B + 2Jx_B(1 - x_B) \\ - \frac{1}{2}\left(\Delta E^0 - T\Delta S^0 + J\right) + RT\ln\frac{2}{e} + \varphi(T) \end{aligned} \tag{8}$$

A similar result can be obtained by considering Eq. 5b as a condition of the minimum of free energy with respect to x_B and integrating it along this variable:

$$\begin{aligned} F = RT(x_B\ln(x_B) + (1 - x_B)\ln(1 - x_B)) \\ + \left(\Delta E^0 - T\Delta S^0\right)x_B + 2Jx_B(1 - x_B) - RT + \varphi(T) \end{aligned} \tag{9}$$

Equations 8 and 9 coincide with the functional of free energy of MSM in the approximation of binary interactions (the excess energy being double the interaction constant [4]) that adequately describes many one-step gradual and abrupt transition curves. For these cases IHM and MSM may thus be considered as formally identical.

Two-sublattice model

The two-step spin crossover requires two sublattices (α and β with equal number of centres) for its description thus creating a new situation. Each α centre is surrounded by β centres and, vice versa, each β centre is surrounded by α centres. In the mean-field approximation the total Hamiltonian is substituted by two one-centre Hamiltonians [12]:

$$\mathcal{H}_\alpha = \frac{\Delta E^0}{2}\boldsymbol{\sigma}_\alpha - \left(J_\alpha\langle\sigma_\alpha\rangle + J_{\alpha\beta}\langle\sigma_\beta\rangle\right)\boldsymbol{\sigma}_\alpha \tag{10}$$

$$\mathcal{H}_\beta = \frac{\Delta E^0}{2}\boldsymbol{\sigma}_\beta - \left(J_\beta\langle\sigma_\beta\rangle + J_{\alpha\beta}\langle\sigma_\alpha\rangle\right)\boldsymbol{\sigma}_\beta \tag{11}$$

in which mean values of fictitious spins $\langle\sigma_\alpha\rangle$ and $\langle\sigma_\beta\rangle$ are proportional to the populations of corresponding sublattices by HS molecules

$$\langle\sigma_\alpha\rangle = 2\frac{N_B(\alpha)}{{}^1\!/\!_2N} - 1;\ \langle\sigma_\beta\rangle = 2\frac{N_B(\beta)}{{}^1\!/\!_2N} - 1 \tag{12}$$

where $N_B(\alpha)$ and $N_B(\beta)$ are numbers of molecules B in α and β centres, respectively, $N = N_A + N_B$ is the total number of centres. According to Eq. 12 the sum of mean fictitious spins reflects the composition of the mixture:

$$\frac{1}{2}(\langle\sigma_\alpha\rangle + \langle\sigma_\alpha\rangle) = x_B - x_A \tag{13}$$

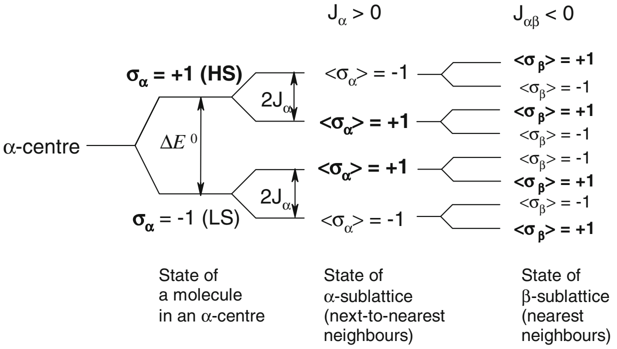

Fig. 2 Energy level diagram of a molecule in an α centre of the crystal described by the Hamiltonians defined in Eqs. 11 and 12

The energy level diagram corresponding to this case is shown in Fig. 2. In this approach the state of each sublattice is considered separately; however, the energy of a given molecule in a given centre depends of the population of both sublattices. A similar diagram can be drawn for a molecule in a β centre.

Taking into account the assumed positions of α and β centres one might suppose that the constants J_α and J_β characterise next-to-nearest neighbour interactions, whereas the constant $J_{\alpha\beta}$ refers to the nearest neighbour interactions [14]. This interpretation can only be used with a certain proviso. The objections are twofold: firstly the estimates of J_α and J_β obtained by regression of experimental two-step transition curves are positive and larger than the magnitude of the negative $J_{\alpha\beta}$; secondly, the cases of $J_\alpha = J_\beta$ and $J_\alpha \neq J_\beta$ yield fundamentally different types of transition curves.

Let us consider this problem in detail. Solutions of Eqs. 10 and 11 can be written as:

$$\ln\frac{1 + \langle\sigma_\alpha\rangle}{1 - \langle\sigma_\alpha\rangle} + \frac{\Delta E^0 - T\Delta S^0 - 2J_\alpha\langle\sigma_\alpha\rangle - 2J_{\alpha\beta}\langle\sigma_\beta\rangle}{RT} = 0 \tag{14}$$

$$\ln\frac{1 + \langle\sigma_\beta\rangle}{1 - \langle\sigma_\beta\rangle} + \frac{\Delta E^0 - T\Delta S^0 - 2J_\beta\langle\sigma_\beta\rangle - 2J_{\alpha\beta}\langle\sigma_\alpha\rangle}{RT} = 0 \tag{15}$$

Testing theoretical models of two-step spin crossover can be advantageously done using experimental data on transitions in $[Fe(2\text{-pic})_3]Cl_2\cdot EtOH$ [19] obtained by Mössbauer spectroscopy and remaining up to now the standard of accuracy ($\pm 1\%_m$).

In the approximation $J_\alpha = J_\beta$ Eqs. 14 and 15 yield theoretical curves qualitatively correct but not adequately describing experimental data (Fig. 3, first row in Table 1). Populations of sublattices are generally equal $\left(\langle\sigma_\alpha\rangle = \langle\sigma_\beta\rangle\right)$

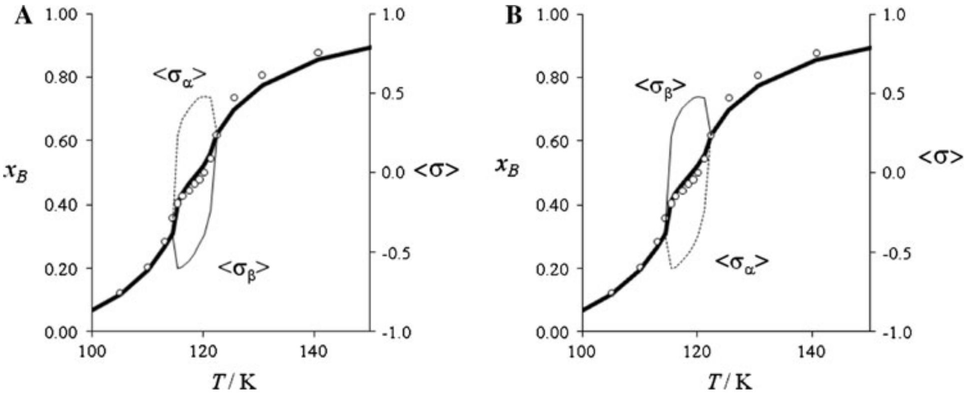

Fig. 3 Two solutions of IHM describing (*thick solid line* $x_B(T)$) experimental transition curve of spin crossover in $[Fe(2\text{-pic})_3]Cl_2 \cdot EtOH$ obtained by solving Eqs. 14 and 15 in the approximation $J_\alpha = J_\beta$ (first row in Table 1). *Thin lines* are mean fictitious spins

Table 1 Estimates of parameters of IHM obtained by regression of experimental data on spin crossover in $[Fe(2\text{-pic})_3]Cl_2 \cdot EtOH$ [19]

	Condition	Regr. err.	$T_{1/2}$ (K)	J_α (kJ/mol)	J_β (kJ/mol)	$J_{\alpha\beta}$ (kJ/mol)	Notes
1	$J_\alpha = J_\beta$	0.023	119.1 ± 0.2	$J_\alpha = J_\alpha = 0.877 \pm 0.003$		−0.196 ± 0.019	$\langle\sigma_\alpha\rangle < \langle\sigma_\beta\rangle$ $\langle\sigma_\alpha\rangle > \langle\sigma_\beta\rangle$
2	$J_\alpha \neq J_\beta$	0.011	118.5 ± 0.13	834 ± 0.012	0.987 ± 0.017	−0.184 ± 0.005	$\langle\sigma_\alpha\rangle > \langle\sigma_\beta\rangle$
3		0.049*	118.5	834	0.987	−0.184	$\langle\sigma_\alpha\rangle < \langle\sigma_\beta\rangle$ non-optimised
4		0.011	118.5 ± 0.13	0.987 ± 0.017	834 ± 0.012	−0.184 ± 0.005	$\langle\sigma_\alpha\rangle < \langle\sigma_\beta\rangle$
5		0.049*	118.5	834	0.987	−0.184	$\langle\sigma_\alpha\rangle > \langle\sigma_\beta\rangle$ non-optimised

$T_{1/2} = \Delta E^0/\Delta S^0$; $\Delta E^0 = 6.14$ kJ/mol was fixed according to calorimetric data [21]

* Computed using the number of degrees of freedom $f = M-4$, in which M is the number of points

except in a narrow range of temperatures in which, under the condition $1/2(J_\alpha + J_\beta) - J_{\alpha\beta} > RT_{1/2}$, populations *spontaneously* become unequal $\langle\sigma_\alpha\rangle \neq \langle\sigma_\beta\rangle$, i.e. certain ordering spontaneously appears in the distribution molecules over sublattices. This model has two fully equivalent solutions corresponding to preferential population of either α or β centres by HS molecules (Fig. 3).

When $J_\alpha \neq J_\beta$ the populations of sublattices are unequal in the whole range of temperatures i.e. certain ordering exists at all temperatures and in fact at any $J_\alpha \neq J_\beta$ including negative values. In this approximation Eqs. 14 and 15 yield two adequate solutions differing by the mirror image values of J_α, J_β and by the sign of $\langle\sigma_\alpha\rangle - \langle\sigma_\beta\rangle$ (second and fourth rows in Table 1, Figs. 4a and 5a). At low temperatures and $J_\alpha < J_\beta$ the population of α sublattice is larger than that of β sublattice $\langle\sigma_\alpha\rangle > \langle\sigma_\beta\rangle$; however, when temperature reaches the right end of the region of spontaneous ordering the difference $\langle\sigma_\alpha\rangle - \langle\sigma_\beta\rangle$ changes its sign (Fig. 4a, second row in Table 1). When $J_\beta < J_\alpha$ the pattern is inversed: at low temperatures $\langle\sigma_\alpha\rangle < \langle\sigma_\beta\rangle$ (Fig. 5a, the fourth row in Table 1). Each set of parameters also allows another solution distinguished by the inverse sign of $\langle\sigma_\alpha\rangle - \langle\sigma_\beta\rangle$, which, however, yields inadequate description of experimental data (third and fifth rows in Table 1, Figs. 4b, 5b). These solutions change the sign of $\langle\sigma_\alpha\rangle - \langle\sigma_\beta\rangle$ at the left end of the region of spontaneous ordering. They can easily be lost in the process of optimisation of parameters merely because of their inadequacy. Beyond the region of spontaneous ordering adequate and inadequate solutions coincide.

We see that when intrasublattice interaction constants are unequal one of the sublattices is preferentially occupied by HS molecules in the whole range of temperatures. The region of spontaneous ordering is distinguished by higher difference in populations of sublattices.

Taking this into account one can conclude that inequality of intrasublattice interaction constants reflects *different affinities* of sublattices towards molecules of a given kind.

Retracing our steps back we can conclude that IHM takes into account next-to-nearest neighbour interactions by introducing affinities of sublattices towards molecules of a given kind.

Mean values of fictitious spins can be expressed in terms of the composition on degree of order of the Gorsky–Bragg–Williams approximation of ordering (see e.g. in [20]):

$$s_B = 2\frac{N_B(\beta)}{Nx_B} - 1 \tag{16}$$

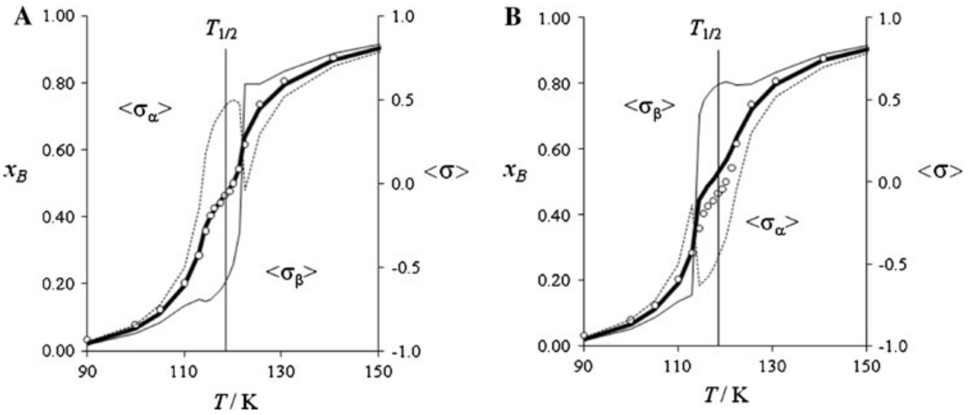

Fig. 4 Two solutions of IHM describing (*thick solid line* $x_{\mathrm{B}}(T)$) experimental transition curve of spin crossover in [Fe(2-pic)$_3$]Cl$_2$·EtOH [19] obtained by solving Eqs. 14 and 15 in the approximation $J_\alpha < J_\beta$ (**a** second and **b** third rows in Table 1). *Thin lines* are mean fictitious spins

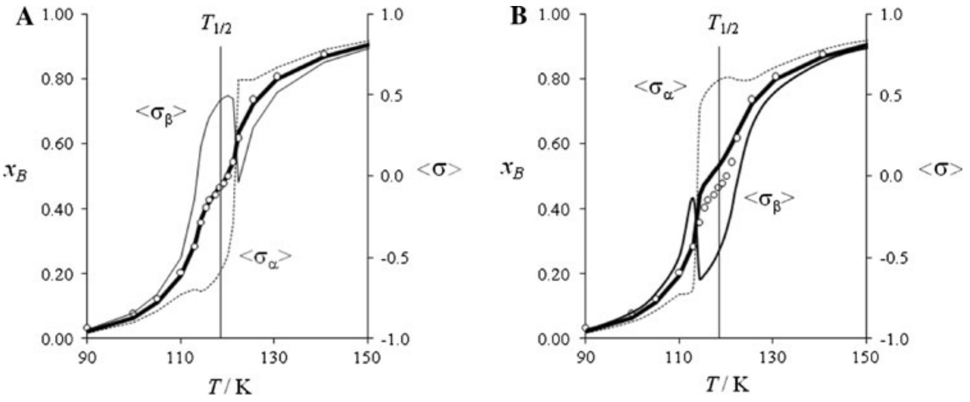

Fig. 5 Two solutions of IHM describing (*thick solid line* $x_{\mathrm{B}}(T)$) experimental transition curve of spin crossover in [Fe(2-pic)$_3$]Cl$_2$·EtOH [19] obtained by solving Eqs. 14 and 15 in the approximation $J_\alpha > J_\beta$ (**a** fourth and **b** fifth rows in Table 1). *Thin lines* are mean fictitious spins

However, the derivation of the functional of free energy can be more advantageously done by employing the probabilities $u_{\alpha\mathrm{B}}$ and $u_{\beta\mathrm{B}}$ of finding α and β centres, respectively, occupied by a molecule B:

$$u_{\alpha\mathrm{B}} = (1 - s_{\mathrm{B}})x_{\mathrm{B}};\ u_{\beta\mathrm{B}} = (1 + s_{\mathrm{B}})x_{\mathrm{B}} \tag{17}$$

From Eqs. 12, 16, and 17 one obtains:

$$\langle\sigma_\alpha\rangle = 2u_{\alpha\mathrm{B}} - 1;\ \langle\sigma_\beta\rangle = 2u_{\beta\mathrm{B}} - 1 \tag{18}$$

Taking into account that $u_{\alpha\mathrm{B}} + u_{\alpha\mathrm{A}} = 1$ and $u_{\beta\mathrm{B}} + u_{\beta\mathrm{A}} = 1$ it can be concluded that mean values of fictitious spins equal the difference of probabilities of finding a centre of a given sublattice to be occupied by HS and LS molecules:

$$\langle\sigma_\beta\rangle = u_{\beta\mathrm{B}} - u_{\beta\mathrm{A}} \quad \langle\sigma_\alpha\rangle = u_{\alpha\mathrm{B}} - u_{\alpha\mathrm{A}} \tag{19}$$

It must however be mentioned that $\langle\sigma_\alpha\rangle$ and $\langle\sigma_\beta\rangle$ reflect the probability to find B-molecule in a centre of a *selected sublattice*. The probability of finding a centre taken at random occupied by a molecule B equals its mole fraction x_{B}:

$$u_{\mathrm{B}} = \frac{1}{2}\left(u_{\alpha\mathrm{B}} + u_{\beta\mathrm{B}}\right) = x_{\mathrm{B}} \tag{20}$$

In the case of a single lattice the probability of finding a centre occupied by the molecule B coincides with its mole fraction x_{B}, providing thus for the identity of IHM and MSM in the description of the one-step spin crossover.

Let us analyse the case of two-step spin crossover by deriving the functional of free energy of the IHM. Consider Eqs. 14 and 15 as conditions of the minimum of free energy with respect to probabilities $u_{\alpha\mathrm{B}}$ and $u_{\beta\mathrm{B}}$:

$$\left(\frac{\partial F}{\partial u_{\alpha\mathrm{B}}}\right)_{T,u_{\beta\mathrm{B}}} = RT\ln\frac{u_{\alpha\mathrm{B}}}{(1-u_{\alpha\mathrm{B}})} - T\Delta S^0 + \Delta E^0 + 2J_\alpha + 2J_{\alpha\beta} - 4J_\alpha u_{\alpha\mathrm{B}} - 4J_{\alpha\beta}u_{\beta\mathrm{B}} = 0 \tag{21}$$

$$\left(\frac{\partial F}{\partial u_{\beta\mathrm{B}}}\right)_{T,u_{\alpha\mathrm{B}}} = RT\ln\frac{u_{\beta\mathrm{B}}}{(1-u_{\beta\mathrm{B}})} - T\Delta S^0 + \Delta E^0 + 2J_\beta + 2J_{\alpha\beta} - 4J_\beta u_{\beta\mathrm{B}} - 4J_{\alpha\beta}u_{\alpha\mathrm{B}} = 0. \tag{22}$$

Integrating Eq. 22 along $u_{\alpha\mathrm{B}}$, and Eq. 23 along $u_{\beta\mathrm{B}}$ yields:

$$\begin{aligned} F &= \int \frac{\partial F}{\partial u_{\alpha \mathrm{B}}} du_{\alpha \mathrm{B}} \\ &= RT(u_{\alpha \mathrm{B}} \ln u_{\alpha \mathrm{B}} + (1 - u_{\alpha \mathrm{B}}) \ln(1 - u_{\alpha \mathrm{B}}) - 1) \\ &\quad + \left(\Delta F^0 + 2J_\alpha + 2J_{\alpha\beta}\right) u_{\alpha \mathrm{B}} - 2J_\alpha u_{\alpha \mathrm{B}}^2 \\ &\quad - 4J_{\alpha\beta} u_{\beta \mathrm{B}} u_{\alpha \mathrm{B}} + f\left(u_{\beta \mathrm{B}}, T\right) \end{aligned} \tag{23}$$

$$\begin{aligned} F &= \int \frac{\partial F}{\partial u_{\beta \mathrm{B}}} \mathrm{d}u_{\beta \mathrm{B}} \\ &= RT\left(u_{\beta \mathrm{B}} \ln u_{\beta \mathrm{B}} + \left(1 - u_{\beta \mathrm{B}}\right) \ln\left(1 - u_{\beta \mathrm{B}}\right) - 1\right) \\ &\quad + \left(\Delta F^0 + 2J_\beta + 2J_{\alpha\beta}\right) u_{\beta \mathrm{B}} - 2J_\beta u_{\beta \mathrm{B}}^2 - 4J_{\alpha\beta} u_{\beta \mathrm{B}} u_{\beta \mathrm{B}} \\ &\quad + \varphi(u_{\alpha \mathrm{B}}, T) \end{aligned} \tag{24}$$

The nature of $f(u_{\beta \mathrm{B}}, T)$ and $\varphi(u_{\alpha \mathrm{B}}, T)$ becomes obvious when comparing Eqs. 23 and 24 and taking into account that the functional F is the same in both equations:

$$\begin{aligned} f\left(u_{\beta B}, T\right) &= RT\left(u_{\beta \mathrm{B}} \ln u_{\beta \mathrm{B}} + \left(1 - u_{\beta \mathrm{B}}\right) \ln\left(1 - u_{\beta \mathrm{B}}\right)\right) \\ &\quad - RT + \left(\Delta F^0 + 2J_\beta + 2J_{\alpha\beta}\right) u_{\beta \mathrm{B}} - 2J_\beta u_{\beta \mathrm{B}}^2 \\ \varphi(u_{\alpha B}, T) &= RT(u_{\alpha \mathrm{B}} \ln u_{\alpha \mathrm{B}} + (1 - u_{\alpha \mathrm{B}}) \ln(1 - u_{\alpha \mathrm{B}})) \\ &\quad - RT + \left(\Delta F^0 + 2J_\alpha + 2J_{\alpha\beta}\right) u_{\alpha \mathrm{B}} - 2J_\alpha u_{\alpha \mathrm{B}}^2 \end{aligned} \tag{25}$$

Substituting these defined functions in either Eq. 23 or Eq. 24 yields:

$$\begin{aligned} F &= RT(u_{\alpha \mathrm{B}} \ln u_{\alpha \mathrm{B}} + (1 - u_{\alpha \mathrm{B}}) \ln(1 - u_{\alpha \mathrm{B}}) \\ &\quad + u_{\beta \mathrm{B}} \ln u_{\beta \mathrm{B}} + \left(1 - u_{\beta \mathrm{B}}\right) \ln\left(1 - u_{\beta \mathrm{B}}\right)\big) - 2RT \\ &\quad + \left(\Delta F^0 + 2J_\alpha + 2J_{\alpha\beta}\right) u_{\alpha \mathrm{B}} + \left(\Delta F^0 + 2J_\beta + 2J_{\alpha\beta}\right) u_{\beta \mathrm{B}} \\ &\quad - 2J_\alpha u_{\alpha \mathrm{B}}^2 - 2J_\beta u_{\beta \mathrm{B}}^2 - 4J_{\alpha\beta} u_{\beta \mathrm{B}} u_{\alpha \mathrm{B}} \end{aligned} \tag{26}$$

Expressing in Eq. 26 the probabilities $u_{\alpha \mathrm{B}}$ and $u_{\beta \mathrm{B}}$ via x_{B} and s_{B}, one obtains the following functional of free energy derived form the mean-field solutions of IHM:

$$\begin{aligned} \frac{1}{2} F &= \frac{RT}{2} \begin{pmatrix} (1 - s_{\mathrm{B}}) x_{\mathrm{B}} \ln(1 - s_{\mathrm{B}}) x_{\mathrm{B}} \\ + (1 - (1 - s_{\mathrm{B}}) x_{\mathrm{B}}) \ln(1 - (1 - s_{\mathrm{B}}) x_{\mathrm{B}}) \\ + (1 + s_{\mathrm{B}}) x_{\mathrm{B}} \ln(1 + s_{\mathrm{B}}) x_{\mathrm{B}} \\ + (1 - (1 + s_{\mathrm{B}}) x_{\mathrm{B}}) \ln(1 - (1 + s_{\mathrm{B}}) x_{\mathrm{B}}) \end{pmatrix} - RT \\ &\quad + \left(\Delta F^0 + 2J_{\alpha\beta} + J_\alpha + J_\beta + \left(J_\beta - J_\alpha\right) s_{\mathrm{B}}\right) x_{\mathrm{B}} \\ &\quad - \left(J_\alpha + J_\beta + 2J_{\alpha\beta} + 2\left(J_\beta - J_\alpha\right) s_{\mathrm{B}}\right. \\ &\quad \left. + \left(J_\alpha + J_\beta - 2J_{\alpha\beta}\right) s_{\mathrm{B}}^2\right) x_{\mathrm{B}}^2 + \varphi(T) \end{aligned} \tag{27}$$

The first term in Eq. 27 coincides with the configurational entropy of the MSM functional [17], i.e. of the ordered binary mixture in the approximation of Gorsky–Bragg–Williams:

$$\begin{aligned} F &= \frac{RT}{2} \begin{pmatrix} (1 - s_{\mathrm{B}}) x_{\mathrm{B}} \ln(1 - s_{\mathrm{B}}) x_{\mathrm{B}} \\ + (1 - (1 - s_{\mathrm{B}}) x_{\mathrm{B}}) \ln(1 - (1 - s_{\mathrm{B}}) x_{\mathrm{B}}) \\ + (1 + s_{\mathrm{B}}) x_{\mathrm{B}} \ln(1 + s_{\mathrm{B}}) x_{\mathrm{B}} \\ + (1 - (1 + s_{\mathrm{B}}) x_{\mathrm{B}}) \ln(1 - (1 + s_{\mathrm{B}}) x_{\mathrm{B}}) \end{pmatrix} \\ &\quad + \left(\Delta E_{\mathrm{ex}} + \Delta^{\mathrm{A}} + \Delta F^0\right) x_{\mathrm{B}} - \left[2\Delta^{\mathrm{A}} - \Delta^{\mathrm{B}} + \Delta E_{\mathrm{ex}}\right. \\ &\quad \left. + \left(\Delta^{\mathrm{B}} - \Delta F_{\mathrm{ex}}\right) s_{\mathrm{B}}^2\right] x_{\mathrm{B}}^2 + \left(1 - s_{\mathrm{B}}^2\right)\left(\Delta^{\mathrm{A}} - \Delta^{\mathrm{B}}\right) x_{\mathrm{B}}^3 + \text{const.} \end{aligned} \tag{28}$$

in which ΔE_{ex} and $\Delta^{\mathrm{A(B)}}$ are interaction parameters that can be expressed via molecular binary potentials (φ_{ij}) and perturbations of binary potentials by third bodies ($\sum \alpha^k \varphi_{ij}$). Thus, for the diamond lattice the following has been obtained [17]:

$$\begin{aligned} \Delta E_{\mathrm{ex}} &= 4(2\varphi_{\mathrm{AB}} - \varphi_{\mathrm{BB}} - \varphi_{\mathrm{AA}}) \\ &\quad + 12\left(\left(\alpha^{\mathrm{A}} + \alpha^{\mathrm{B}}\right)\varphi_{\mathrm{AB}} - \alpha^{\mathrm{B}}\varphi_{\mathrm{BB}} - \alpha^{\mathrm{A}}\varphi_{\mathrm{AA}}\right) \end{aligned} \tag{29}$$

$$\Delta^{\mathrm{A}} = -12\left(\alpha^{\mathrm{A}} - \alpha^{\mathrm{B}}\right)\left(\varphi_{\mathrm{AA}} - \varphi_{\mathrm{AB}}\right) \tag{30}$$

$$\Delta^{\mathrm{B}} = -12\left(\alpha^{\mathrm{A}} - \alpha^{\mathrm{B}}\right)\left(\varphi_{\mathrm{AB}} - \varphi_{\mathrm{BB}}\right). \tag{31}$$

Polynomial parts of the functionals defined in Eqs. 27 and 28 do not coincide: IHM yields free energy as a function of both s_{B} and s_{B}^2, whereas in MSM it depends on s_{B}^2 alone. However, in the approximation $J_\alpha = J_\beta$ the functional defined in Eq. 27 is reduced to:

$$\begin{aligned} \frac{1}{2} F &= \frac{RT}{2} \begin{pmatrix} (1 - s_{\mathrm{B}}) x_{\mathrm{B}} \ln(1 - s_{\mathrm{B}}) x_{\mathrm{B}} \\ + (1 - (1 - s_{\mathrm{B}}) x_{\mathrm{B}}) \ln(1 - (1 - s_{\mathrm{B}}) x_{\mathrm{B}}) \\ + (1 + s_{\mathrm{B}}) x_{\mathrm{B}} \ln(1 + s_{\mathrm{B}}) x_{\mathrm{B}} \\ + (1 - (1 + s_{\mathrm{B}}) x_{\mathrm{B}}) \ln(1 - (1 + s_{\mathrm{B}}) x_{\mathrm{B}}) \end{pmatrix} - RT \\ &\quad + \left(\Delta F^0 + 2J_{\alpha\beta} + 2J\right) x_{\mathrm{B}} \\ &\quad - \left(2J + 2J_{\alpha\beta} + \left(2J - 2J_{\alpha\beta}\right) s_{\mathrm{B}}^2\right) x_{\mathrm{B}}^2 + \text{const} \end{aligned} \tag{32}$$

which is equivalent to the MSM functional under the condition $\Delta = \Delta^{\mathrm{A}} = \Delta^{\mathrm{B}} \neq 0$:

$$\begin{aligned} F &= \frac{RT}{2} \begin{pmatrix} (1 - s_{\mathrm{B}}) x_{\mathrm{B}} \ln(1 - s_{\mathrm{B}}) x_{\mathrm{B}} \\ + (1 - (1 - s_{\mathrm{B}}) x_{\mathrm{B}}) \ln(1 - (1 - s_{\mathrm{B}}) x_{\mathrm{B}}) \\ + (1 + s_{\mathrm{B}}) x_{\mathrm{B}} \ln(1 + s_{\mathrm{B}}) x_{\mathrm{B}} \\ + (1 - (1 + s_{\mathrm{B}}) x_{\mathrm{B}}) \ln(1 - (1 + s_{\mathrm{B}}) x_{\mathrm{B}}) \end{pmatrix} \\ &\quad + \left(\Delta F^0 + \Delta E_{\mathrm{ex}} + \Delta\right) x_{\mathrm{B}} \\ &\quad - \left[\Delta + \Delta E_{\mathrm{ex}} + (\Delta - \Delta E_{\mathrm{ex}}) s_{\mathrm{B}}^2\right] x_{\mathrm{B}}^2 + \text{const} \end{aligned} \tag{33}$$

From the point of view of MSM this case is rather specific if not impossible: according to the model of molecular interactions on which the functional defined in Eq. 28 is based the condition $\Delta^{A} = \Delta^{B} \neq 0$ means zero interchange energy:

$$2\varphi_{AB} - \varphi_{AA} - \varphi_{BB} = 0 \quad \text{i.e.} \quad \varphi_{AB} = \frac{\varphi_{AA} + \varphi_{BB}}{2} \tag{34}$$

All interaction parameters of MSM then become equal.

$$\Delta^{A} = \Delta^{B} = \Delta E_{ex} = 6\left(\alpha^{A} - \alpha^{B}\right)\left(\varphi_{BB} - \varphi_{AA}\right). \tag{35}$$

Terms containing the degree of order disappear and such a model no longer reproduces the two-step spin crossover. We see that MSM, being based on a certain scheme of molecular interactions, does not allow some combinations of formal parameters. On the other hand IHM, being based on the concept of the field connected with the crystal lattice, allows the equality of intrasublattice interaction constants and allows independent variations of J_{α}, J_{β}, and $J_{\alpha\beta}$.

Equations 14 and 15 can also be written in terms of composition and degree of order:

$$\begin{aligned} &RT\ln\frac{(x_B - s_B x_B)}{(1 - x_B + s_B x_B)} + \Delta F^{0} + 2\left(J_{\alpha} + J_{\alpha\beta}\right) \\ &\quad - 4\left(J_{\alpha} + J_{\alpha\beta}\right)x_B + 4\left(J_{\alpha} - J_{\alpha\beta}\right)s_B x_B \\ &\quad = 0 \end{aligned} \tag{36}$$

$$\begin{aligned} &RT\ln\frac{(1 + s_B)x_B}{(1 - (1 + s_B)x_B)} + \Delta F^{0} + 2\left(J_{\beta} + J_{\alpha\beta}\right) \\ &\quad - 4\left(J_{\beta} + J_{\alpha\beta}\right)x_B - 4\left(J_{\beta} - J_{\alpha\beta}\right)s_B x_B \\ &\quad = 0. \end{aligned} \tag{37}$$

However, the integration of Eqs. 36 and 37 along x_B and s_B yields incomparable functionals of free energy. This originates from the fact that IHM intrinsically defines mean values of fictitious spins as independent variables and then the composition and degree of order are not independent:

$$4x_B s_B = \langle\sigma_{\beta}\rangle - \langle\sigma_{\alpha}\rangle \tag{38}$$

On the other hand if we consider x_B and s_B as independent then $\langle\sigma_{\alpha}\rangle$ and $\langle\sigma_{\beta}\rangle$ are interrelated:

$$\langle\sigma_{\alpha}\rangle + \langle\sigma_{\beta}\rangle = 4x_B - 2; \tag{39}$$

This also concerns the physical meaning of the minimisation procedures underlying these models. The independence of x_B and s_B means that the overall composition of the system and the distribution of molecules over odd and even centres vary in order to achieve the minimum of free energy in both sublattices. The independence of fictitious spins means that the composition of each sublattice minimises the energy in each sublattice separately.

On the other hand it is possible to derive conditions of equilibrium for the functional defined in Eq. 27 assuming x_B and s_B as independent variables:

$$\begin{aligned} \frac{1}{2}\left(\frac{\partial F}{\partial x_B}\right)_{s_B} = {} & \frac{RT}{2}\left((1 + s_B)\ln\frac{(1 + s)x_B}{1 - (1 + s_B)x_B}\right. \\ & \left. + (1 - s_B)\ln\frac{(1 - s_B)x_B}{1 - (1 - s_B)x_B}\right) - T\Delta S^{0} \\ & + \Delta E^{0} + J_{\alpha} + J_{\beta} + 2J_{\alpha\beta} + \left(J_{\beta} - J_{\alpha}\right)s_B \\ & - 2\left[J_{\alpha} + J_{\beta} + 2J_{\alpha\beta} + 2\left(J_{\beta} - J_{\alpha}\right)s_B\right. \\ & \left. + \left(J_{\alpha} + J_{\beta} - 2J_{\alpha\beta}\right)s_B^{2}\right]x_B = 0 \end{aligned} \tag{40}$$

$$\begin{aligned} \frac{1}{2}\left(\frac{\partial F}{\partial s_B}\right)_{x_B} = {} & \frac{RTx_B}{2}\ln\frac{(1 + s_B)(1 - (1 - s_B)x_B)}{(1 - s_B)(1 - (1 + s_B)x_B)} \\ & + \left(J_{\beta} - J_{\alpha}\right)x_B \\ & - 2\left[J_{\beta} - J_{\alpha} + \left(J_{\alpha} + J_{\beta} - 2J_{\alpha\beta}\right)s_B\right]x_B^{2} \\ = {} & 0. \end{aligned} \tag{41}$$

Despite the marked difference between systems of Eqs. 36, 37 and 40, 41, they yield identical theoretical curves $x_B(T)$ and $s_B(T)$. This originates from the actual form of partial derivatives $\partial u_{\alpha(\beta)B}/\partial x_B$, $\partial u_{\alpha(\beta)B}/\partial s_B$. It is well known that:

$$\left(\frac{\partial F}{\partial x_B}\right)_{s_B} = \left(\frac{\partial F}{\partial u_{\alpha B}}\right)_{u_{\beta B}}\left(\frac{\partial u_{\alpha B}}{\partial x_B}\right)_{s_B} + \left(\frac{\partial F}{\partial u_{\beta B}}\right)_{u_{\alpha B}}\left(\frac{\partial u_{\beta B}}{\partial x_B}\right)_{s_B} \tag{42}$$

$$\left(\frac{\partial F}{\partial s_B}\right)_{x_B} = \left(\frac{\partial F}{\partial u_{\alpha B}}\right)_{u_{\beta B}}\left(\frac{\partial u_{\alpha B}}{\partial s_B}\right)_{x_B} + \left(\frac{\partial F}{\partial u_{\beta B}}\right)_{u_{\alpha B}}\left(\frac{\partial u_{\beta B}}{\partial s_B}\right)_{x_B}. \tag{43}$$

Taking into account that:

$$\begin{aligned} &\left(\frac{\partial u_{\alpha B}}{\partial x_B}\right)_{s_B} = 1 - s_B; \; \left(\frac{\partial u_{\beta B}}{\partial x_B}\right)_{s_B} = 1 + s_B; \\ &\left(\frac{\partial u_{\alpha B}}{\partial s_B}\right)_{x_B} = -x_B; \; \left(\frac{\partial u_{\beta B}}{\partial s_B}\right)_{x_B} = +x_B \end{aligned} \tag{44}$$

yields:

$$\begin{aligned} \left(\frac{\partial F}{\partial x_B}\right)_{s_B} = {} & \left(\frac{\partial F}{\partial u_{\alpha B}}\right)_{u_{\beta B}} + \left(\frac{\partial F}{\partial u_{\beta B}}\right)_{u_{\alpha B}} \\ & + s_B\left[\left(\frac{\partial F}{\partial u_{\beta B}}\right)_{u_{\alpha B}} - \left(\frac{\partial F}{\partial u_{\alpha B}}\right)_{u_{\beta B}}\right] \end{aligned} \tag{45}$$

$$\left(\frac{\partial F}{\partial s_B}\right)_{x_B} = x_B\left[\left(\frac{\partial F}{\partial u_{\beta B}}\right)_{u_{\alpha B}} - \left(\frac{\partial F}{\partial u_{\alpha B}}\right)_{u_{\beta B}}\right]. \tag{46}$$

According to Eqs. 45 and 46 zero values of $\partial F/\partial u_{\alpha B}$ and $\partial F/\partial u_{\beta B}$ imply $\partial F/\partial x_B = 0$ and $\partial F/\partial x_B = 0$ (and vice versa).

Table 2 Estimates of parameters of the free energy functional defined in Eq. 27, describing spin crossover in $[Fe(2\text{-pic})_3]Cl_2{\cdot}EtOH$ [19]

	Condition	Regr. err.	$T_{1/2}$ (K)	J_α (kJ/mol)	J_β (kJ/mol)	$J_{\alpha\beta}$ (kJ/mol)	Search for s_B	Fig.
1	$J_\alpha = J_\beta$	0.022	119.1 ± 0.2	0.872 ± 0.017		0.198 ± 0.011	Downwards and upwards	6a, b
2	$J_\alpha \neq J_\beta$	0.011	118.5 ± 0.1	0.834 ± 0.013	0.987 ± 0.017	0.184 ± 0.004	Upwards	7a
3		0.043	–	–	–	–	Downwards	7b
4		0.011	118.5 ± 0.1	0.987 ± 0.017	0.834 ± 0.013	0.184 ± 0.004	Downwards	7c
5		0.043	–	–	–	–	Upwards	7d

$T_{1/2} = \Delta E^0/\Delta S^0$; $\Delta E^0 = 6.14$ kJ/mol was fixed according to calorimetric data [21]

Indeed experimental transition curves of spin crossover in $[Fe(2\text{-pic})_3]Cl_2{\cdot}EtOH$ [19] can be parameterised by the system defined in Eqs. 40 and 41 yielding estimates of parameters coinciding (within the reliability intervals) with those obtained by solving Eqs. 14 and 15 (cf. Tables 1, 2). For identical sets of parameters (ΔE^0, $T_{1/2}$, J_α, J_β, $J_{\alpha\beta}$) theoretical curves $x_B(T)$ and $s_B(T)$ obtained from Eqs. 40 and 41, Figs. 6 and 7 coincide with those computed by using Eqs. 21 and 22 with the accuracy corresponding to the chosen accuracy of numerical solution.

Specific properties of obtained solutions remain unaltered: when $J_\alpha = J_\beta$ the degree of order is generally zero except in the region of spontaneous ordering (Fig. 6; Table 2). Two equivalent solutions exist corresponding to positive and negative degrees of order. When $J_\alpha \neq J_\beta$ two mirror symmetrical sets of J_α and J_β adequately describe experimental data (Fig. 7a, c; second and fourth rows in Table 2) yielding non-zero degree of order in the whole range of temperatures. For each of these sets there is an additional solution with opposite signs of the degree of order, however, yielding inadequate descriptions of experimental data (Fig. 7b, d; third and fifth rows in Table 2). Similarly to the initial IHM solutions, s_B changes its sign at the border of the region of spontaneous ordering and it is impossible to combine solutions achieving one-sign s_B in the whole range of temperature.

Conclusions

IHM is based on the concept of field connected with the crystal lattice that binds molecules and provides for the preferential population of sublattices by molecules of a given kind. MSM is based on the concept of molecular interactions (binary and many-body) that yields a functional of free energy different form that of IHM.

Different ways of accounting for the energy of molecular interactions yield different polynomial expansions of free energy over composition and degree of order. On the other hand both models show similar contributions from the configurational entropy arising from the configurational entropy of the ordered binary mixture in the approximation of Gorsky–Bragg–Williams.

Independent variables in IHM are fictitious spins or probabilities of finding a centre of sublattice occupied by a molecule of a given kind. This means that equilibrium conditions are controlled by the energy minima for each sublattice separately. In MSM, the overall composition of the degrees of order are chosen as independent variables hence equilibrium corresponds to the global minimum of free energy with respect to composition and distribution of molecules over sublattices.

The choice of independent variables on the one hand is strongly bound to the basic concept of the model, hence the

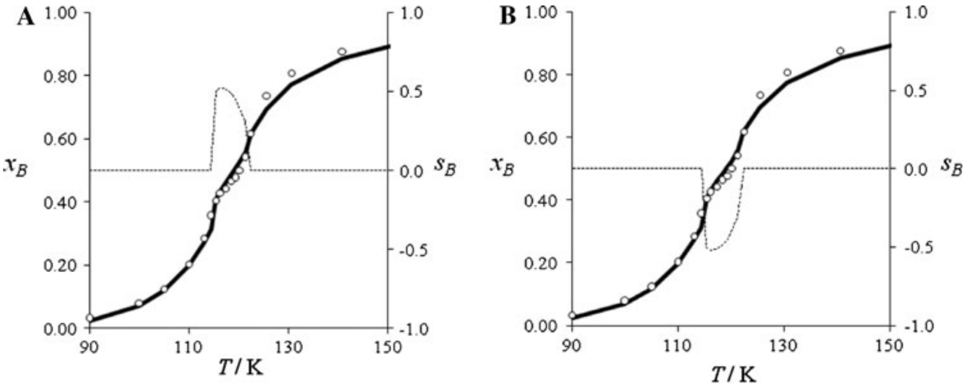

Fig. 6 Description (*thick solid line* $x_B(T)$) of spin crossover in $[Fe(2\text{-pic})_3]Cl_2{\cdot}EtOH$ [19] obtained by solving Eqs. 40 and 41 in the approximation $J_\alpha = J_\beta$ searching for solution from $s_B = 1$ downwards (**a**) and from $s_B = -1$ upwards (**b**); *thin dashed line* represents the degree of order s_B. Estimates of parameters are given in Table 2. Details of mathematical procedures are given in section "Methods"

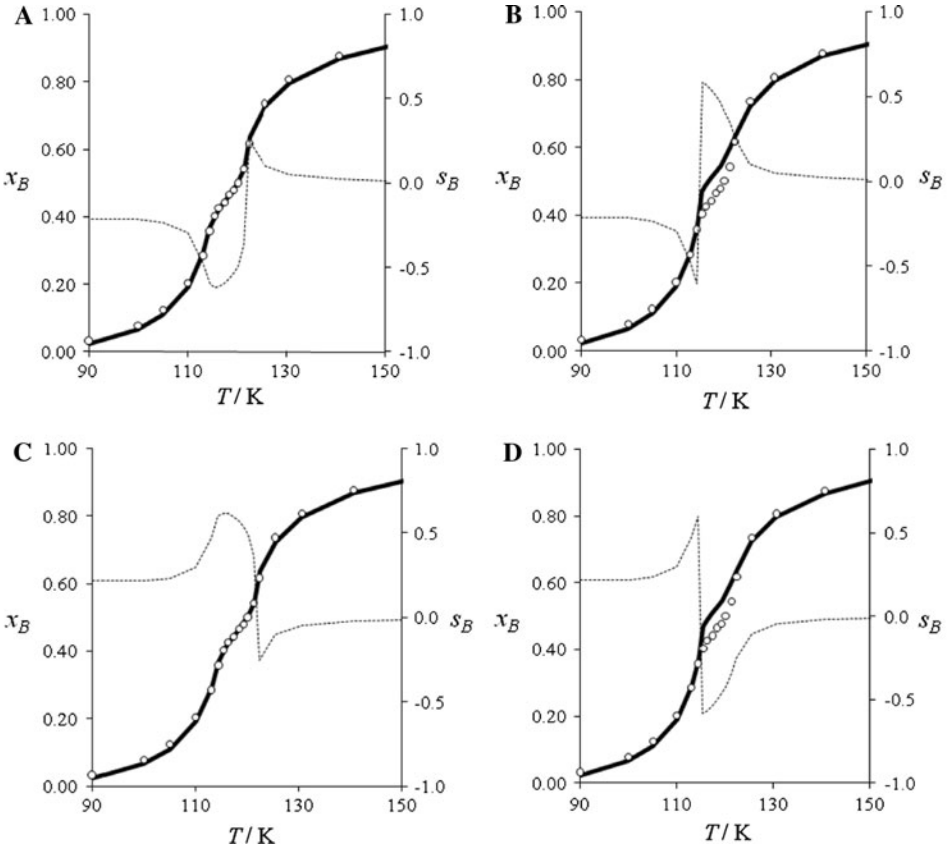

Fig. 7 Description (*thick solid line* $x_{\mathrm{B}}(T)$) of spin crossover in [Fe(2-pic)$_3$]Cl$_2$·EtOH [19] obtained by solving Eqs. 40 and 41 in the approximation $J_\alpha \neq J_\beta$ searching for solution from $s_{\mathrm{B}} = 1$ downwards (**b**, **c**) and from $s_{\mathrm{B}} = -1$ upwards (**a**, **d**); *thin dashed line* represents the degree of order s_{B}. Estimates of parameters are given in Table 2. Details of mathematical procedures are given in section "Methods"

form of the actual functional. On the other hand, purely formally, a given functional can be written via any set of these variables. Conditions of equilibrium thus obtained yield identical theoretical curves because of the actual form of the interdependence between fictitious spins, composition and degree of order.

IHM in the approximation $J_\alpha = J_\beta$ predicts the experimentally observed spontaneous ordering; however, it does not provide for adequate description of experimental transition curve and can therefore be neglected.

The choice between IHM in the approximation $J_\alpha \neq J_\beta$ and MSM cannot be made on the basis of available data because regressional errors yielded by these models for the most accurate experimental data on the two-step spin crossover [19] are statistically indistinguishable ($\sigma_{yx} = 0.008$ for MSM and $\sigma_{yx} = 0.11$ for IHM [4]). Some evidence in favour of MSM proceeds from the spontaneous ordering [22] predicted by this model. However, up to now we only have rather qualitative experimental data on the degree of order in spin-crossover systems.

Therefore, at present the choice of the model is determined by the possibility of rational interpretation of the estimates of parameters. From the analysis given above it follows that IHM interaction constants are formal parameters characterising sublattices, hence not related to molecular properties. MSM parameters, on the contrary, have been introduced by employing certain models of molecular interactions and can be expressed in terms of binary and many-body potentials. This makes MSM attractive for chemists working on the synthesis of promising spin-crossover compounds.

Methods

Methods of numerical solution of equations derived from the functional of free energy of MSM have been discussed in our previous publications [15–18]. Slightly modified versions of these methods have been used in the present investigation. Mean values of fictitious spins are not always rising functions of temperature therefore a consecutive search for solutions is inapplicable for solving Eqs. 14 and 15 of the initial IHM corresponding to heating and cooling modes. Therefore, the Newton–Gauss procedure for solving these equations has been inserted into a multipurpose optimisation program, as explained in [23]. Depending on the initial approximation $\left(\langle\sigma_\alpha\rangle > \langle\sigma_\beta\rangle \text{or} \langle\sigma_\alpha\rangle < \langle\sigma_\beta\rangle\right)$ different solutions discussed above have been obtained.

Conditions of equilibrium defined in Eqs. 40 and 41 derived from the free energy functional defined in Eq. 27

with respect to x_B and s_B allow for the realisation of the consecutive search for solution (similar to that used in MSM [17]). Such a procedure has been inserted into the optimisation program thus yielding transition curves in heating (search for x_B upwards) and cooling (search for x_B downwards) modes as well as searching for s_B upwards and downwards. For the considered set of data transition curves in heating and cooling modes coincide within the regression error;[1] however, when other experimental data exhibiting hysteresis are to be analysed, this approach (taking into account complete equivalence of the functional defined in Eq. 27 and the Ising-like Hamiltonian) might become useful.

The functional defined in Eq. 27 contains terms with odd powers of s_B; therefore the region of negative s_B is not a mirror reflection of the region of positive degrees of order characteristic for MSM. Therefore, searching for solutions has been done in the range $s_B = \pm 1$. Negative values of the degree of order $s_B = 2p_B - 1 < 0$ mean that the probability p_B of a molecule B getting into a β centre is less than 1/2, i.e. ordering is realised by distributing B molecules preferentially over α centres and not over β centres as is usually assumed in the Gorsky–Bragg–Williams approximation of ordering. Changing the sign of $\langle \sigma_{\alpha(\beta)} \rangle$ or s_B (Figs. 5, 7) at the borders of the region of spontaneous ordering thus means a change of the initial assumptions (selection rules) of the actual description of the phenomenon of ordering with no apparent physical explanation.

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References

1. Guetlich P, Goodwin HA (2004) Top Curr Chem 233:1
2. Blundell SJ (2006) Lect Notes Phys 697:345
3. Murray KS (2009) Aust J Chem 62:1081
4. Koudriavtsev AB, Linert W (2010) Zh Strukt Khim 51:364
5. Wenbin L, Rieter JW, Taylor KML (2009) Angew Chem Int Ed 48:650
6. Bodenthin Y, Kurth DG, Schwarz G (2008) Chem Unserer Zeit 42:256
7. Gaspar AB, Munoz MC, Real JA (2006) J Mater Chem 16:2522
8. Hauser A (2004) Top Curr Chem 233:49
9. Paulsen H, Trautwein AX (2004) Top Curr Chem 235:197
10. Wajnflasz J (1970) Phys Status Solid 40:537
11. Bari R, Sivardiere J (1972) Phys Rev B 5:4466
12. Zelentsov VV, Lapushkin GL, Sobolev SS, Shipilov VI (1986) Dokl AN SSSR, Ser Khim 289:393
13. Bousseksou A, Nasser J, Linares J, Boukheddaden K, Varret F (1992) J Phys I France 2:1381
14. Nishino M, Boukheddaden K, Miyashita S, Varret F (2005) Polyhedron 24:2852
15. Koudriavtsev AB (1999) Chem Phys 241:109
16. Koudriavtsev AB, Stassen AF, Haasnoot JG, Grunert M, Weinberger P, Linert W (2003) Phys Chem Chem Phys 5:3666
17. Koudriavtsev AB, Jameson RF, Linert W (2006) Monatsh Chem 137:1283
18. Koudriavtsev AB, Linert W (2009) MATCH Commun Math Comput Chem 62:5
19. Koeppen H, Mueller EW, Koehler CP, Spiering H, Meissner E, Guetlich P (1982) Chem Phys Lett 91:348
20. Moelwyn-Hughes EA (1970) Physikalische Chemie. Georg Thieme Verlag, Stuttgart
21. Sorai M (2002) J Chem Thermodyn 34:1207
22. Chernyshov D, Hostettler M, Törnroos KW, Bürgi HB (2003) Angew Chem Int Ed 42:3825
23. Kudryavtsev AB, Linert W (1996) Physico-chemical applications of NMR. World Scientific Publishers, Singapore

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[1] Heating mode yields a smaller but statistically indistinguishable regression error than the cooling mode ($\sigma_{yx} = 0.107$ and 0.125, respectively). Curves in Figs. 6 and 7 have been obtained in the heating mode.