

# The Role of Binary and Many-Centre Molecular Interactions in Spin Crossover in the Solid State. Part IV. Ordering in Systems with Many-Body Interactions

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**Summary.** The theoretical formalism of solid-state spin crossover taking into account many-body interactions and ordering has been extended to the case of 5-centre interactions in a diamond lattice leading to the splitting of the free energy levels into quintets. Consecutive simplification of the obtained equations has been achieved for multiplets with regularly varying splittings: the variation according to the polynomial of the third order corresponds to 5-centre interactions; quadratic and linear variations yield the formalisms of quaternary and ternary interactions respectively; equidistant multiplets correspond to the model of binary interactions. These types of variations have been deduced from a simple microscopic model of the influence of the external molecule on the considered interaction. Parameters of the developed formalism have been expressed in terms of binary potentials and relative efficiencies of external molecules. The expressions obtained provided an adequate description of experimental two-step spin crossover curves. The formalism developed in this way was found to be similar, but not identical, to the phenomenological description based on the *Landau* theory. Odd power terms in composition (not entering the expansion of free energy derived from *Landau* theory) were found to be generally non-zero and vital for obtaining adequate descriptions of experimental data.

**Keywords.** Spin crossover; Many-body interactions; Ordering.

## Introduction

Spin crossover equilibrium between HS and LS isomers of transition metal complexes [1] is a perfect test system for checking theoretical descriptions of

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chemical reactions in the solid state. Spin crossover has been described employing quantum chemical DFT calculations [2–5] as well as the models of the *Ising*-like Hamiltonian [6–9] and regular solution theory [10]. Parameters of the latter two formalisms have been expressed in terms of the model of a continuum within the theory of elastic interactions [11, 12]. The latter model considers microscopic objects (a molecule or a reaction centre) as perturbations within macroscopic elastic media and thus introduces macroscopically long-range forces between molecules as an initial assumption. A purely phenomenological description of spin crossover involving higher order terms in the expansion of free energy has been derived [13] employing the *Landau* theory of phase transitions.

These formalisms successfully predict general features of all known types of experimental spin crossover transition curves, however they generally fail at the quantitative parameterisation of the most interesting two-step transitions. As has been pointed out [14], models of regular solutions and *Ising*-like Hamiltonian, “although physically transparent, merely squeeze many competing interactions into the Procrustes bed of one phenomenological parameter in an oversimplified model”.

Quantitative description of the two-step spin crossover has been achieved [15–21] within two approximations, *viz.* the model of ternary<sup>a</sup> interactions [15] and the quasi-chemical model [17]. The latter is applicable to systems with strong correlations (such as in polynuclear spin crossover compounds) whereas the former can be applied to systems of weakly interacting mononuclear spin crossover complexes.

The model of weak interactions is based on taking into account the effects of two nearest neighbours on the partition function of a given molecule thus leading to the splitting of free energy levels into triplets. The expressions obtained for the free energy of a binary reaction mixture contain terms cubic and quadratic with respect to mol fractions. The cubic term is connected with ternary interactions characterised by asymmetries of splittings ( $\Delta_1^A, \Delta_1^B$ ) whereas the quadratic term characterised by main splittings ( $D_A, D_B$ ) was assumed to arise from binary interactions. Under simplifying conditions this model can be reduced to that of the regular solution theory with excess energy being equal to the sum of main splittings:

$$\Delta E_{ex} = D_A + D_B.$$

One of the cooperative phenomena observed in spin crossover is the abrupt spin crossover (sometimes accompanied with hysteresis) that is connected with the separation of HS-rich and LS-rich phases. According to the model of ternary interactions [19] abrupt spin crossover can be observed when

$$\Delta E_{ex} + \Delta^{A(B)} > 2RT_{1/2}$$

<sup>a</sup> In our previous publications [15–21] we introduced 3-centre interactions as “triple interactions”. However the term “ternary interactions” seems to be more widely used. Higher order interactions will be called: “quaternary” (4-centre), quintary (5-centre), and so forth. In order to quantitatively characterise them we have introduced “primary”, “secondary”, and “tertiary” effects of external molecules on binary interactions

in which  $T_{1/2} = \Delta E^0 / \Delta S^0$  is the temperature of half-conversion. Abrupt spin crossover thus requires large positive excess energies and/or asymmetries of splittings. Another critical phenomenon: the two-step spin crossover is connected with *ordering* in a binary mixture, *i.e.* with the formation of sub-lattices of A and B isomers. According to the model of ternary interactions ordering occurs [19] when

$$\Delta^{A(B)} - \Delta E_{ex} > RT_{1/2},$$

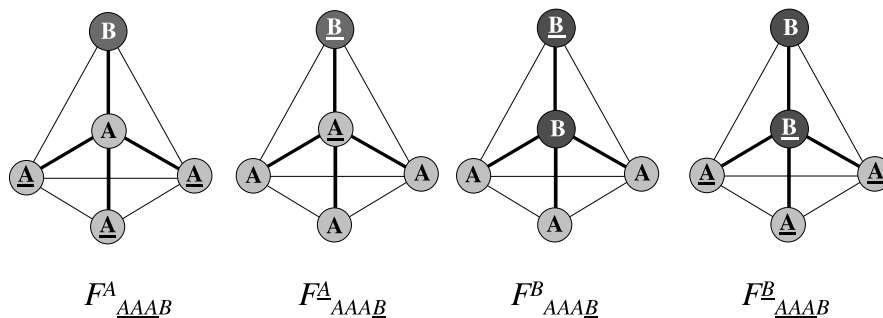
*i.e.* at large negative excess energies. Sharp two-step transitions arise from a combination of negative excess energies and the positive effects of ternary interactions  $\Delta^{A(B)}$ . Negative excess energy can be interpreted as arising from the higher stability of HS-LS pairs compared to HS-HS and LS-LS pairs. Positive asymmetries arise from either specific binary interactions (such as HS→LS charge transfer) or specific relationship between ternary potentials [20].

Strictly speaking the formalism of ternary interactions is only applicable to one-dimensional chains in which ternary and binary interactions alone are important. However, the derived equations successfully describe complicated cases of two-step spin crossover in 2D and 3D systems [15–17]. The reason why this is possible is not obvious because some one-step transition curves require taking into account a larger number of neighbours [19]. Corresponding formalism was derived [19] without taking into account the phenomenon of ordering, *i.e.* for the cases of large positive excess energies. Interaction of a given molecule with  $n$  neighbours splits free energy levels into multiplets of the order  $n + 1$ . The pattern of splittings was characterised by two main splittings ( $D_{A(B)}$ ) and  $2(n - 1)$  asymmetries ( $\Delta_i^{A(B)}$ ).

This paper presents the derivation of the equation for free energy for systems with many-body interactions taking into account the phenomenon of ordering. In order to avoid cumbersome equations the case of tetrahedral environments will be considered whereas the results for octahedral structures will be given only in the final form in the Appendix. First a general equation for free energy in a diamond lattice with ordering will be derived. Then we shall analyse patterns of energy levels arising from taking into account binary, ternary, quaternary, and 5-centre interactions. The corresponding equation for free energy will be derived and the effect of higher order interactions on the shape of transition curves of spin crossover will be analysed. Some examples of the fitting of experimental transition curves to the derived equations will be given thereafter and eventually we compare the presented formalism with that based on *Landau* theory.

### Derivation of the Equation for Free Energy

Let us consider a binary mixture of molecules A and B (LS and HS isomers of a spin crossover compound, respectively) in a diamond lattice with tetrahedral arrangement of nearest neighbours. In this lattice one can select two sub-lattices built of  $\alpha$  and  $\beta$  centres so that every  $\alpha$  centre is surrounded by four  $\beta$  centres and *vice versa*;  $N = N_A + N_B$  centres of such a crystal are then divided into  $N/2$   $\alpha$ -centres and  $N/2$   $\beta$ -centres. The main simplification of the *Bragg-Williams* model



**Fig. 1.** Examples of possible configurations around central molecules A and B

**Table 1.** Probabilities ( $p_A, p_B$ ) to find molecules A and B in  $\alpha$ - and  $\beta$ -centres and corresponding mol fractions ( $X_A, X_B$ ) according to Refs. [15, 18]

	$p_A$	$p_B$	$X_A$	$X_B$
$\alpha$ -centre	$p_A = u_1 = (1 + s)x_A$	$p_B = 1 - u_1$	$X_A = \frac{1}{2}u_1$	$X_B = \frac{1}{2}(1 - u_1)$
$\beta$ -centre	$p_{\underline{A}} = u_2 = (1 - s)x_A$	$p_{\underline{B}} = 1 - u_2$	$X_{\underline{A}} = \frac{1}{2}u_2$	$X_{\underline{B}} = \frac{1}{2}(1 - u_2)$

amounts to the suggestion that molecules A and B are *randomly distributed* among the  $\alpha$  and  $\beta$  centres. The ordering in such a system can be quantitatively characterised by the *degree of order*,  $s = 2p - 1$ , the probability  $p$  of a molecule A to get into an  $\alpha$ -centre being  $p = N_A(\alpha)/N_A$ .

We assume the molecules to be pseudo-independent, *i.e.* we suppose that molecular interactions contribute to energy and probably affect vibrational frequencies but do not change the configurational entropy. Before applying the *Bragg-Williams* approximation we consider molecules A and B in ‘proper’ (A in  $\alpha$  and B in  $\beta$ ) and ‘improper’ ( $\underline{A}$  in  $\beta$  and  $\underline{B}$  in  $\alpha$ ) centres (Fig. 1; also see in Refs. [15, 18]). The probabilities ( $p$ ) to find molecules in these centres and corresponding mol fractions ( $X$ ) are given in Table 1.

The contributions of pseudo-independent molecules A and B towards the free energy are

$$x_A F^A = X_A (p_{\underline{A}}^4 F_{AAAA}^A + 4p_{\underline{A}}^3 p_B F_{AAAB}^A + 6p_{\underline{A}}^2 p_B^2 F_{AABB}^A + 4p_{\underline{A}} p_B^3 F_{ABBB}^A + p_B^4 F_{BBBB}^A) \\ + X_{\underline{A}} (p_A^4 F_{AAAA}^A + 4p_A^3 p_{\underline{B}} F_{AAAB}^A + 6p_A^2 p_{\underline{B}}^2 F_{AABB}^A + 4p_A p_{\underline{B}}^3 F_{ABBB}^A + p_{\underline{B}}^4 F_{BBBB}^A) \quad (1)$$

$$x_B F^B = X_B (p_{\underline{A}}^4 F_{AAAA}^B + 4p_{\underline{A}}^3 p_B F_{AAAB}^B + 6p_{\underline{A}}^2 p_B^2 F_{AABB}^B + 4p_{\underline{A}} p_B^3 F_{ABBB}^B + p_B^4 F_{BBBB}^B) \\ + X_{\underline{B}} (p_A^4 F_{AAAA}^B + 4p_A^3 p_{\underline{B}} F_{AAAB}^B + 6p_A^2 p_{\underline{B}}^2 F_{AABB}^B + 4p_A p_{\underline{B}}^3 F_{ABBB}^B + p_{\underline{B}}^4 F_{BBBB}^B) \quad (2)$$

Let us consider the contribution of molecules A, supposing that the nature of the centre does not affect individual free energies (*Bragg-Williams* type approximation,  $F_{AAAA}^A = F_{AAAA}^A$ ,  $F_{AAAB}^A = F_{AAAB}^A$ , *etc.*) then the free energy level is split into a *quintet* ( $F_{AAAA}^A, F_{AAAB}^A, F_{AABB}^A, F_{ABBB}^A, F_{BBBB}^A$ ). By referring all free energies to  $F_{AAAA}^A$  we

introduce (see Fig. 2 below) individual splittings of the free energy levels  $J_i^A$ :

$$\begin{aligned} F_{AAAB}^A &= F_{AAAA}^A + J_1^A, & F_{AABB}^A &= F_{AAAA}^A + J_1^A + J_2^A, \\ F_{ABBB}^A &= F_{AAAA}^A + J_1^A + J_2^A + J_3^A, & F_{BBBB}^A &= F_{AAAA}^A + D_A \end{aligned} \quad (3)$$

*i.e.*  $D_A = J_1^A + J_2^A + J_3^A + J_4^A$

This yields:

$$\begin{aligned} x_A F^A &= X_A F_{AAAA}^A + 4(X_{AP_A}^3 p_B + X_{AP_A}^3 p_B) J_1^A + 6(X_{AP_A}^2 p_B^2 + X_{AP_A}^2 p_B^2)(J_1^A + J_2^A) \\ &+ 4(X_{AP_A} p_B^3 + X_{AP_A} p_B^3)(J_1^A + J_2^A + J_3^A) + (X_{AP_B}^4 + X_{AP_B}^4) D_A \end{aligned} \quad (4)$$

Expressing the probabilities  $p_A$  and mol fractions  $X_A$  in terms of  $x_A$  and  $s$  according to Table 1 we get:

$$\begin{aligned} x_A F^A &= x_A F_{AAAA}^A + 4(1-s^2)x_A^2((1+s^2)x_A^2 - (1+3s^2)x_A^3)J_1^A \\ &+ 6(1-s^2)x_A^2(x_A - 2(1+s^2)x_A^2 + (1+3s^2)x_A^3)(J_1^A + J_2^A) \\ &+ 4(1-s^2)x_A^2(1-3x_A + 3(1+s^2)x_A^2 - (1+3s^2)x_A^3)(J_1^A + J_2^A + J_3^A) \\ &+ (x_A + (1-s^2)x_A^2(-4+6x_A - 4(1+s^2)x_A^2 + (1+3s^2)x_A^3))D_A \end{aligned} \quad (5)$$

By introducing small parameters in the form of asymmetries of splittings  $\Delta_i^A = 4J_i^A - D_A$  one obtains:

$$x_A F^A = x_A F_{AAAA}^A + a_5 x_A^5 + a_4 x_A^4 + a_3 x_A^3 + a_2 x_A^2 + a_1 x_A \quad (6)$$

$$\begin{aligned} a_5 &= (1-s^2)(1+3s^2)(-\frac{1}{2}\Delta_1^A + \frac{1}{2}\Delta_2^A - \Delta_3^A); a_4 = (1-s^4)(+\Delta_1^A + 3\Delta_3^A) \\ a_3 &= (1-s^2)(-\frac{3}{2}\Delta_1^A - \frac{3}{2}\Delta_2^A - 3\Delta_3^A); a_2 = (1-s^2)(\Delta_1^A + \Delta_2^A + \Delta_3^A - D_A) \\ a_1 &= D_A \end{aligned} \quad (6a)$$

Similarly the contribution of molecules B can be derived as:

$$x_B F^B = x_B F_B + b_5 x_A^5 + b_4 x_A^4 + b_3 x_A^3 + b_2 x_A^2 + b_1 x_A \quad (7)$$

in which:

$$\begin{aligned} b_5 &= (1-s^2)(1+3s^2)(+\frac{1}{2}\Delta_1^B - \frac{1}{2}\Delta_2^B + \Delta_3^B) \\ b_4 &= -\frac{3}{2}\Delta_1^B + \frac{5}{2}\Delta_2^B - 2\Delta_3^B + s^2(-3\Delta_1^B + 3\Delta_2^B - 6\Delta_3^B) + s^4(+\frac{1}{2}\Delta_1^B - \frac{3}{2}\Delta_2^B) \\ b_3 &= +\frac{5}{2}\Delta_1^B - \frac{7}{2}\Delta_2^B + \Delta_3^B + s^2(+\frac{3}{2}\Delta_1^B - \frac{9}{2}\Delta_2^B + 3\Delta_3^B) \\ b_2 &= -\frac{5}{2}\Delta_1^B + \frac{3}{2}\Delta_2^B - D_B + s^2(-\frac{1}{2}\Delta_1^B + \frac{3}{2}\Delta_2^B + D_B) \\ b_1 &= +\Delta_1^B + D_B \\ \Delta_i^B &= 4J_i^B - D_B \end{aligned} \quad (7a)$$

Combining Eqs. (6) and (7) and adding configurational entropy (see Ref. [18]) we obtain:

$$\begin{aligned} F &= x_A F_{AAAA}^A + (1-x_A)F_{BBBB}^B + c_5 x_A^5 + c_4 x_A^4 + c_3 x_A^3 + c_2 x_A^2 + c_1 x_A \\ &+ \frac{1}{2} NkT [u_1 \ln u_1 + (1-u_1) \ln(1-u_1) + u_2 \ln u_2 + (1-u_2) \ln(1-u_2)] \end{aligned} \quad (8)$$

in which:

$$\begin{aligned}
c_5 &= +(1-s^2)(1+3s^2)\left(-\frac{1}{2}\Delta_1^A + \frac{1}{2}\Delta_2^A - \Delta_3^A + \frac{1}{2}\Delta_1^B - \frac{1}{2}\Delta_2^B + \Delta_3^B\right) \\
c_4 &= \Delta_1^A + 3\Delta_3^A - \frac{3}{2}\Delta_1^B + \frac{5}{2}\Delta_2^B - 2\Delta_3^B + s^2(-3\Delta_1^B + 3\Delta_2^B - 6\Delta_3^B) \\
&\quad + s^4\left(-\Delta_1^A - 3\Delta_3^A + \frac{1}{2}\Delta_1^B - \frac{3}{2}\Delta_2^B\right) \\
c_3 &= -\frac{3}{2}\Delta_1^A - \frac{3}{2}\Delta_2^A - 3\Delta_3^A + \frac{5}{2}\Delta_1^B - \frac{7}{2}\Delta_2^B + \Delta_3^B \\
&\quad + \left(\frac{3}{2}\Delta_1^A + \frac{3}{2}\Delta_2^A + 3\Delta_3^A + \frac{3}{2}\Delta_1^B - \frac{9}{2}\Delta_2^B + 3\Delta_3^B\right)s^2 \\
c_2 &= \Delta_1^A + \Delta_2^A + \Delta_3^A - \frac{5}{2}\Delta_1^B + \frac{3}{2}\Delta_2^B - D_B - D_A \\
&\quad + (D_B + D_A - \Delta_1^A - \Delta_2^A - \Delta_3^A - \frac{1}{2}\Delta_1^B + \frac{3}{2}\Delta_2^B)s^2 \\
c_1 &= \Delta_1^B + D_A + D_B
\end{aligned} \tag{8a}$$

This equation represents an expansion of free energy into a series of powers of  $x_A$ :

$$\begin{aligned}
F &= A_5x_A^5 + A_4x_A^4 + A_3x_A^3 + A_2x_A^2 + A_1x_A + A_0 \\
&\quad + \frac{1}{2}NkT[u_1 \ln u_1 + (1-u_1) \ln(1-u_1) + u_2 \ln u_2 + (1-u_2) \ln(1-u_2)] \tag{9}
\end{aligned}$$

in which the coefficients  $A_i$  are functions of asymmetries  $\Delta_i^A$ ,  $\Delta_i^B$ , main splittings,  $D_A$ ,  $D_B$ , and even powers of the degree of order  $s$ . Although Eq. (8) can be directly employed in practical simulations, it contains too many adjustable parameters (main splittings and asymmetries) that are not independent. Using asymmetries as formal parameters is also inconvenient because by setting the highest order asymmetry to zero does not cancel the contribution of the highest order interactions<sup>b</sup>. The relationship between asymmetries of different orders will be found in the next section by considering a physical model of many-body interactions.

### Effects of Many-Body Interactions

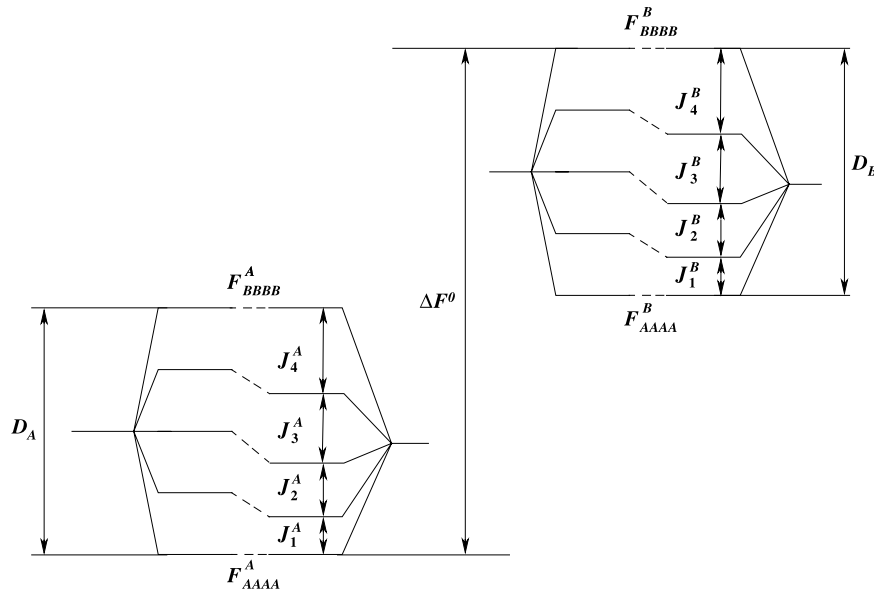
Assuming (for simplicity) the variations of vibrational frequencies, available volume, and electronic degeneracy under the influence of environment to be negligibly small, then we can calculate parameters of Eq. (8) *via* the energies of the central molecule in given surroundings. This can be done employing binary and many-body potentials, the latter describing deviations of these energies from the sum of binary interactions of the central molecule with its nearest neighbours. Splittings of energy levels for the considered case of tetrahedral environment can be written as (see Fig. 2):

$$J_1^A = E_{AAAB}^A - E_{AAAA}^A = \varphi_{AB} - \varphi_{AA} + \psi_{AAAB}^A - \psi_{AAAA}^A \tag{10}$$

$$J_2^A = E_{AABB}^A - E_{AAAB}^A = \varphi_{AB} - \varphi_{AA} + \psi_{AABB}^A - \psi_{AAAB}^A \tag{10a}$$

$$J_3^A = E_{ABBB}^A - E_{AABB}^A = \varphi_{AB} - \varphi_{AA} + \psi_{ABBB}^A - \psi_{AABB}^A \tag{10b}$$

<sup>b</sup> The advantage of the model of ternary interactions is that it employs one type of asymmetry; setting it to zero *does* cancel the contribution of ternary interactions



**Fig. 2.** Transformation of equidistant quintets as a result of taking into account many-body interactions

$$J_4^A = E_{BBBB}^A - E_{ABBB}^A = \varphi_{AB} - \varphi_{AA} + \psi_{BBBB}^A - \psi_{ABBB}^A \quad (10c)$$

$$D_A = E_{BBBB}^A - E_{AAAA}^A = 4\varphi_{AB} - 4\varphi_{AA} + \psi_{BBBB}^A - \psi_{AAAA}^A \quad (10d)$$

in which  $\varphi$  are binary and  $\psi$  are many-body potentials. Relevant asymmetries are:

$$\Delta_1^A = 4J_1^A - D_A = +4\psi_{AAAB}^A - 3\psi_{AAAA}^A - \psi_{BBBB}^A \quad (11)$$

$$\Delta_2^A = 4J_2^A - D_A = +4\psi_{AABB}^A - 4\psi_{AAAB}^A - \psi_{BBBB}^A + \psi_{AAAA}^A \quad (11a)$$

$$\Delta_3^A = 4J_3^A - D_A = +4\psi_{ABBB}^A - 4\psi_{AABB}^A - \psi_{BBBB}^A + \psi_{AAAA}^A \quad (11b)$$

A similar set of equations can be written for energy levels of the central molecule B. These equations show that whereas asymmetries depend purely on the strength of many-body interactions the excess energy  $\Delta E_{ex} = D_A + D_B$  contains contributions from both binary and many-body potentials. As has been shown in Refs. [15, 19] a system with purely binary interactions yields free energy multiplets with equal individual splittings (*i.e.* with zero asymmetries  $\Delta_i^{A(B)} = 0$ ). Taking into account ternary and higher order interactions apparently yields some other *regular* relationship between *unequal* splittings (Fig. 2). This relationship can be found by supposing that many-body interactions are perturbations of binary potentials.

### Ternary Interactions

Let us suppose that the many-body potential arises from effects of third bodies on all pair interactions (Fig. 3):

$$\psi_{A_x B_{4-x}}^{A(B)} = \sum_{k \neq j} \sum_j \varepsilon_{ij}^k \quad (12)$$

in which  $\varepsilon_{ij}^k$  defines the effect of the ‘atom’  $k$  on the ‘bond’  $ij$ .

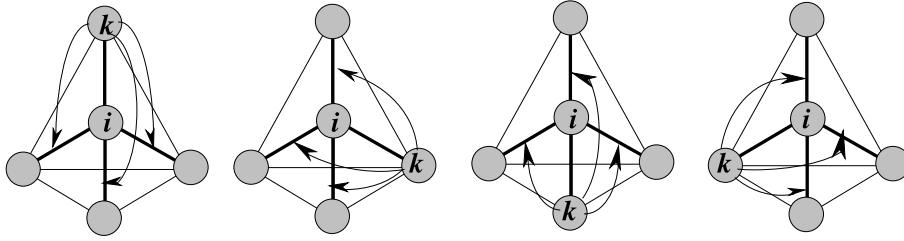


Fig. 3. A model of many-body interactions arising from the effect of the third body

Table 2. Energy levels of a molecule (A) in a tetrahedral environment in terms of binary potentials ( $\varphi_{ij}$ ) and three-centre effects  $\varepsilon_{ij}^k$

	$\varepsilon_{AA}^A$	$\varepsilon_{AB}^A$	$\varepsilon_{AA}^B$	$\varepsilon_{AB}^B$
$E_{AAAA}^A = 4\varphi_{AA} +$	12	0	0	0
$E_{AAAB}^A = 3\varphi_{AA} + \varphi_{AB} +$	6	3	3	0
$E_{AABB}^A = 2\varphi_{AA} + 2\varphi_{AB} +$	2	4	4	2
$E_{ABBB}^A = \varphi_{AA} + 3\varphi_{AB} +$	0	3	3	6
$E_{BBBB}^A = 4\varphi_{AB} +$	0	0	0	12

There are 12 such “primary” many-body effects per tetrahedron (Fig. 3) belonging to four types (Table 2) that can be represented as fractions ( $\alpha^k$ ) of the corresponding binary potential:

$$\varepsilon_{AA}^A = \alpha^A \varphi_{AA}, \quad \varepsilon_{AB}^A = \alpha^A \varphi_{AB}, \quad \varepsilon_{AA}^B = \alpha^B \varphi_{AA}, \quad \varepsilon_{AB}^B = \alpha^B \varphi_{AB} \quad (13)$$

Due to the high symmetry of a perfect tetrahedron (Fig. 3) all homogeneous effects can be assumed to be identical in all environments irrespective their composition: *e.g.* the effect  $\varepsilon_{AB}^A$  can be assumed to be the same in configurations A(AAAB), A(AABB) and A(ABBB)<sup>c</sup>.

According to Table 2, the splittings in multiplets are:

$$D_A = E_{BBBB}^A - E_{AAAA}^A = 4\varphi_{AB} - 4\varphi_{AA} + 12(\varepsilon_{AB}^B - \varepsilon_{AA}^A) \quad (14)$$

<sup>c</sup> In a square-planar configuration one has to distinguish cis- and trans-effects having different magnitudes and probabilities. However, the main results obtained for tetrahedral structures also hold for square-planar ones (see Appendix A1)



$$J_4^A = E_{BBBB}^A - E_{ABBB}^A = \varphi_{AB} - \varphi_{AA} - 3\varepsilon_{AB}^A - 3\varepsilon_{AA}^B + 6\varepsilon_{AB}^B \quad (14a)$$

$$J_3^A = E_{ABBB}^A - E_{AABB}^A = +\varphi_{AB} - \varphi_{AA} - 2\varepsilon_{AA}^A - \varepsilon_{AB}^A - \varepsilon_{AA}^B + 4\varepsilon_{AB}^B \quad (14b)$$

$$J_2^A = E_{AABB}^A - E_{AAAA}^A = \varphi_{AB} - \varphi_{AA} - 4\varepsilon_{AA}^A + \varepsilon_{AB}^A + \varepsilon_{AA}^B + 2\varepsilon_{AB}^B \quad (14c)$$

$$J_1^A = E_{AAAA}^A - E_{AABB}^A = \varphi_{AB} - \varphi_{AA} - 6\varepsilon_{AA}^A + 3\varepsilon_{AB}^A + 3\varepsilon_{AA}^B \quad (14d)$$

All splittings are unequal but finite differences of the first order are constant:

$$d_1^A = J_2^A - J_1^A = J_3^A - J_2^A = J_4^A - J_3^A = 2(\varepsilon_{AA}^A - \varepsilon_{AB}^A - \varepsilon_{AA}^B + \varepsilon_{AB}^B) \quad (15)$$

Or, in terms of  $\alpha^k$  and  $\varphi_{ij}$ :

$$d_1^A = 2(\alpha^A - \alpha^B)(\varphi_{AA} - \varphi_{AB}) \quad (15a)$$

Finite differences of second and third orders are zero and therefore the variation of splittings in such quintets is linear. Similar expressions can be derived for the molecule B. Individual splittings can then be written as:

$$J_i^{A(B)} = J_{i-1}^{A(B)} + \delta_1^{A(B)} = J_1^{A(B)} + (i-1)\delta_1^{A(B)} \quad (16)$$

in which the increments  $\delta_1^{A(B)}$  are:

$$\delta_1^A = 2(\alpha^A - \alpha^B)(\varphi_{AA} - \varphi_{AB}) \quad (17)$$

$$\delta_1^B = 2(\alpha^A - \alpha^B)(\varphi_{AB} - \varphi_{BB}) \quad (18)$$

The excess energy  $E_{ex} = D_A + D_B$  can also be written as a function of binary potentials and effects of third bodies:

$$\begin{aligned} \Delta E_{ex} &= D_B + D_A \\ &= 4(2\varphi_{AB} - \varphi_{BB} - \varphi_{AA}) + 12(\alpha^A\varphi_{AB} - \alpha^B\varphi_{BB} + \alpha^B\varphi_{AB} - \alpha^A\varphi_{AA}) \end{aligned} \quad (19)$$

The asymmetries  $\Delta_i^{A(B)}$  in a quintet with linearly varying  $J_i^{A(B)}$  are given by:

$$\Delta_i^{A(B)} = 4J_i^{A(B)} - D_{A(B)} \quad (20)$$

$$\Delta_i^{A(B)} = (-10 + 4i)\delta_1^{A(B)} \quad (21)$$

*i.e.*

$$\Delta_1^{A(B)} = -6\delta_1^{A(B)}, \quad \Delta_2^{A(B)} = -2\delta_1^{A(B)}, \quad \Delta_3^{A(B)} = +2\delta_1^{A(B)} \quad (22)$$

This linear relationship between  $J_i$  drastically simplifies the expression for free energy (Eq. (8)), it becomes:

$$\begin{aligned} F &= x_A F_{AAAA}^A + (1-x_A)F_{BBBB}^B + c_3 x_A^3 + c_2 x_A^2 + c_1 x_A + \frac{1}{2} NkT [u_1 \ln u_1 \\ &+ (1-u_1) \ln(1-u_1) + u_2 \ln u_2 + (1-u_2) \ln(1-u_2)] \end{aligned} \quad (23)$$

in which:

$$\begin{aligned} c_3 &= 6(\delta_1^A - \delta_1^B)(1-s^2), & c_2 &= 12\delta_1^B - 6\delta_1^A - D_B - D_A + (6\delta_1^A + D_A + D_B)s^2, \\ c_1 &= D_A + D_B - 6\delta_1^B \end{aligned} \quad (23a)$$

As expected, this equation is equivalent to that derived from a simplified model of interactions with two neighbours [19]:

$$\begin{aligned}
 F = & +x_A F_{AAA} + (1 - x_A) F_{BBB} - x_A^3 (1 - s^2) [\Delta_1^A - \Delta_1^B] \\
 & + x_A^2 [(1 - s^2) ((\Delta_1^A - \Delta_1^B) - (\Delta_1^B + D_A + D_B)) - 2s^2 \Delta_1^B] \\
 & + x_A (D_A + D_B + \Delta_1^B) + \frac{1}{2} NkT [u_1 \ln u_1 + (1 - u_1) \ln(1 - u_1) \\
 & + u_2 \ln u_2 + (1 - u_2) \ln(1 - u_2)] \quad (24)
 \end{aligned}$$

Coefficients of Eq. (23) can be directly written in terms of  $\varphi_{AA}$ ,  $\varphi_{BB}$ ,  $\varphi_{AB}$ ,  $\alpha^A$  and  $\alpha^B$  as:

$$\begin{aligned}
 c_3 = & 12(\alpha^A - \alpha^B)(\varphi_{AA} + \varphi_{BB} - 2\varphi_{AB})(1 - s^2) \\
 c_2 = & -4(2\varphi_{AB} - \varphi_{BB} - \varphi_{AA})(1 - s^2)(1 + 3\alpha^B) + 24(\alpha^A - \alpha^B)(\varphi_{AB} - \varphi_{BB}) \quad (25) \\
 c_1 = & 4(2\varphi_{AB} - \varphi_{BB} - \varphi_{AA}) + 12[\alpha^A(\varphi_{BB} - \varphi_{AA}) + 2\alpha^B(\varphi_{AB} - \varphi_{BB})]
 \end{aligned}$$

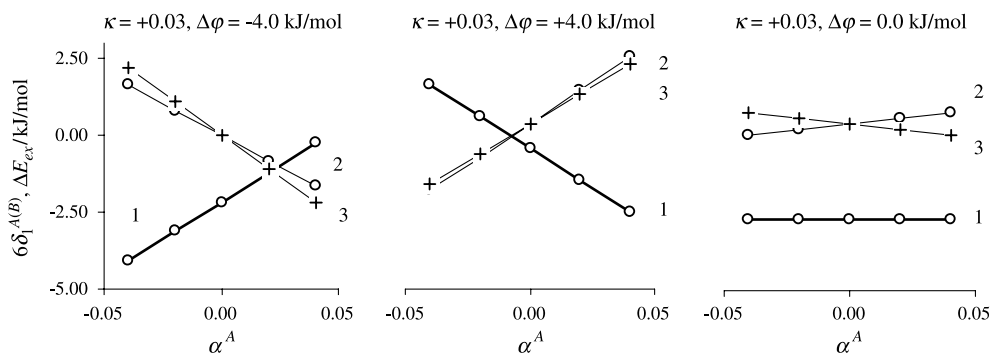
Species in equilibrium (HS and LS molecules) are very similar therefore the magnitudes of  $\alpha^A$  and  $\alpha^B$  should not be very different. One can thus assume  $|\alpha^A| \approx |\alpha^B|$ . However, at the complete equality  $\alpha^A = \alpha^B$  the highest order term in Eq. (25) disappears: primary effects of molecules A and B compensate each other. On the other hand when signs of these effects are opposite ( $\alpha^B \approx -\alpha^A$ , ‘‘anti-compensation’’) the coefficient of the highest order term in Eq. (25) is maximal. Therefore the condition  $\alpha^B = -\alpha^A$  can be used as a regularisation boundary for systems with pronounced effects of many-body interactions.

The number of adjustable parameters can be further reduced by making some assumption concerning binary potentials. One of the homo-molecular potentials can be fixed at some feasible value (e.g.  $\varphi_{BB} = 12$  kJ/mol [20]). The energy of hetero-molecular interactions can be computed according to a modified *Berthelot* rule:

$$\varphi_{AB} = -(1 + \kappa)(\varphi_{AA}\varphi_{BB})^{\frac{1}{2}} \quad (26)$$

**Table 3.** Non-ideality parameters computed from the effects of third molecules on binary interactions in the approximation  $\alpha^B = -\alpha^A$ ;  $\varphi_{BB} = -12$  kJ/mol

$\varphi_{AA} - \varphi_{BB}$ kJ/mol	$\alpha^A$	$\frac{\Delta E_{ex}}{\text{kJ/mol}}$	$\frac{6\delta_1^A}{\text{kJ/mol}}$	$\frac{6\delta_1^B}{\text{kJ/mol}}$	$\frac{\Delta E_{ex}}{\text{kJ/mol}}$	$\frac{6\delta_1^A}{\text{kJ/mol}}$	$\frac{6\delta_1^B}{\text{kJ/mol}}$
		$\kappa = -0.03$			$\kappa = +0.03$		
-4.0	0.040	6.394	-2.457	-1.383	-0.257	-1.659	-2.181
-4.0	0.000	4.474	0.000	0.000	-2.177	0.000	0.000
-4.0	-0.040	2.554	2.457	1.383	-4.097	1.659	2.181
0.0	0.040	2.880	-0.346	0.346	-2.880	0.346	-0.346
0.0	0.000	2.880	0.000	0.000	-2.880	0.000	0.000
0.0	-0.040	2.880	0.346	-0.346	-2.880	-0.346	0.346
4.0	0.04	2.048	1.444	2.396	-2.655	2.008	1.832
4.0	0.000	3.968	0.000	0.000	-0.735	0.000	0.000
4.0	-0.040	5.888	-1.444	-2.396	1.185	-2.008	-1.832



**Fig. 4.** Typical dependencies of non-ideality parameters on relative effects of third bodies ( $\alpha^A$ ,  $\alpha^B = -\alpha^A$ ) for different  $\Delta\varphi = \varphi_{AA} - \varphi_{BB}$  and deviations from *Berthelot's* rule,  $\kappa$ ; thick lines (1) refer to  $\Delta E_{ex}$ , and thin lines refer to  $\delta_1^A$  (2) and  $\delta_1^B$  (3)

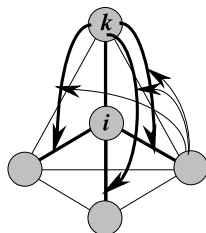
in which  $\kappa$  accounts for specific stabilisation/destabilisation of HS-LS pairs [20]. This leaves us three adjustable non-ideality parameters:  $\varphi_{AA}$ ,  $\kappa$ , and  $\alpha^A$ , that can be reliably estimated from experimental two-step spin crossover curves (similarly to  $\Delta^A$ ,  $\Delta^B$ , and  $\Delta E_{ex}$ ; [15, 16, 19]). Employing  $\alpha^A = -\alpha^B$  and varying  $\varphi_{AA}$  and  $\kappa$  at fixed  $\varphi_{BB}$  one obtains a wide variety of combinations of positive and negative excess energies with positive and negative asymmetries (Table 3, Fig. 4). In agreement with some experimental estimates [15, 19] the values of  $\delta_1^A$  and  $\delta_1^B$  are close to each other but not exactly equal. The combination of negative  $\delta_1^A \approx \delta_1^B$  and negative excess energies required for the simulation of sharp two-step transition curves can be achieved at  $\varphi_{AA} - \varphi_{BB} > 0$  as well as at  $\varphi_{AA} - \varphi_{BB} < 0$ ; however the ratio  $\delta_1^A/\delta_1^B$  in these two cases is different, making the choice of parameters more definite (see also later).

### Quaternary Interactions

Quaternary interactions can be represented as effects of the ( $l \neq k$ )-th particle on effects of the  $k$ -th particle on the neighbouring bond (Fig. 5, Table 4).

These “secondary” effects can be denoted as  $\varepsilon_{ij}^{l(k)}$ , for example,  $\varepsilon_{AA}^{A(B)}$  signifies the contribution towards the many-body potential arising from the particle A changing the effect  $\varepsilon_{AA}^B$ :

$$\psi = \sum_{k \neq j} \sum_j \varepsilon_{ij}^k + \sum_{l \neq k} \sum_{k \neq j} \sum_j \varepsilon_{ij}^{l(k)} \quad (28)$$



**Fig. 5.** Secondary effects of molecules on molecular interactions

**Table 4.** Energy levels of a molecule (A) in a tetrahedral environment in terms of binary potentials ( $\varphi_{ij}$ ) three-centre (primary) effects  $\varepsilon_{ij}^k$ , and four-centre (secondary) effects  $\varepsilon_{ij}^{l(k)}$ 

	$\varepsilon_{AA}^A$	$\varepsilon_{AB}^A$	$\varepsilon_{AA}^B$	$\varepsilon_{AB}^B$	$\varepsilon_{AA}^{A(A)}$	$\varepsilon_{AB}^{A(A)}$	$\varepsilon_{AA}^{A(B)}$	$\varepsilon_{AB}^{A(B)}$	$\varepsilon_{AA}^{B(A)}$	$\varepsilon_{AB}^{B(A)}$	$\varepsilon_{AA}^{B(B)}$	$\varepsilon_{AB}^{B(B)}$
$E_{AAAA}^A = 4\varphi_{AA} +$	12	0	0	0	36	0	0	0	0	0	0	0
$E_{AAAB}^A = 3\varphi_{AA} + \varphi_{AB} +$	6	3	3	0	12	6	9	0	6	3	0	0
$E_{AABB}^A = 2\varphi_{AA} + 2\varphi_{AB} +$	2	4	4	2	2	4	8	4	4	8	4	2
$E_{ABBB}^A = \varphi_{AA} + 3\varphi_{AB} +$	0	3	3	6	0	0	3	6	0	9	6	12
$E_{BBBB}^A = 4\varphi_{AB} +$	0	0	0	12	0	0	0	0	0	0	0	36
$J_1^A = \varphi_{AB} - \varphi_{AA} +$	-6	+3	+3	0	-24	+6	+9	0	+6	+3	0	0
$J_2^A = \varphi_{AB} - \varphi_{AA} +$	-4	+1	+1	+2	-10	-2	-1	+4	-2	+5	+4	+2
$J_3^A = \varphi_{AB} - \varphi_{AA} +$	-2	-1	-1	+4	-2	-4	-5	+2	-4	+1	+2	+10
$J_4^A = \varphi_{AB} - \varphi_{AA} +$	0	-3	-3	+6	0	0	-3	-6	0	-9	-6	+24
$d^1 J_{43} = J_4 - J_3 =$	+2	-2	-2	+2	+2	+4	+2	-8	+4	-10	-8	+14
$d^1 J_{32} = J_3 - J_2 =$	+2	-2	-2	+2	+8	-2	-4	-2	-2	-4	-2	+8
$d^1 J_{21} = J_2 - J_1 =$	+2	-2	-2	+2	+14	-8	-10	+4	-8	+2	+4	+2
$d^2 J_{43} = d^1 J_{43} - d^1 J_{32} =$	0	0	0	0	-6	+6	+6	-6	+6	-6	-6	+6
$d^2 J_{23} = d^1 J_{32} - d^1 J_{21} =$	0	0	0	0	-6	+6	+6	-6	+6	-6	-6	+6

Secondary effects  $\varepsilon_{ij}^{l(k)}$  can be represented as fractions ( $\beta$ ) of primary effects:

$$\varepsilon_{ij}^{l(k)} = \beta^l \varepsilon_{ij}^k = \beta^l \alpha^k \varphi_{ij} \quad (29)$$

There are 36 such secondary effects per tetrahedron, belonging to 8 types (Table 4). Computations according to this scheme yield unequal splittings  $J_1 \neq J_2 \neq J_3 \neq J_4$  and non-zero differences of the second order. Third order differences are zero, manifesting the parabolic variation of splittings:

$$J_i^{A(B)} = J_1^{A(B)} + (i-1)\delta_1^{A(B)} + (i-1)^2\delta_2^{A(B)} \quad (30)$$

in which:

$$\delta_1^A = (\alpha^A - \alpha^B)(\varphi_{AA} - \varphi_{AB})(2 - 3(\beta^B - \beta^A)) + 2\alpha^A[\beta^A(7\varphi_{AA} - 4\varphi_{AB}) - \beta^B(4\varphi_{AA} - \varphi_{AB})] - 2\alpha^B[\beta^A(5\varphi_{AA} - \alpha^B\beta^A 2\varphi_{AB}) - \beta^B(2\varphi_{AA} + \varphi_{AB})] \quad (31)$$

$$\delta_1^B = (\alpha^B - \alpha^A)(\varphi_{BB} - \varphi_{AB})(2 - 3(\beta^A - \beta^B)) + 2\alpha^B[\beta^B(7\varphi_{BB} - 4\varphi_{AB}) - \beta^A(4\varphi_{BB} - \varphi_{AB})] - 2\alpha^A[\beta^B(5\varphi_{BB} - 2\varphi_{AB}) - \beta^A(2\varphi_{BB} + \varphi_{AB})] \quad (32)$$

$$\delta_2^A = 3(\beta^B - \beta^A)(\alpha^A - \alpha^B)(\varphi_{AA} - \varphi_{AB}) \quad (33)$$

$$\delta_2^B = 3(\beta^B - \beta^A)(\alpha^A - \alpha^B)(\varphi_{BB} - \varphi_{AB}) \quad (34)$$

The asymmetries and main splittings can then be derived in terms of  $\delta_1^{A(B)}$  and  $\delta_2^{A(B)}$  as:

$$D_{A(B)} = 4J_1^{A(B)} + 6\delta_1^{A(B)} + 14\delta_2^{A(B)} \quad (35)$$

$$\Delta_i^{A(B)} = -10(\delta_1^{A(B)} + \delta_2^{A(B)}) + 4i(\delta_1^{A(B)} - 2\delta_2^{A(B)}) + 4i^2\delta_2^{A(B)} \quad (36)$$

*i.e.*:

$$\begin{aligned}\Delta_1^{A(B)} &= -6\delta_1^{A(B)} - 14\delta_2^{A(B)}, & \Delta_2^{A(B)} &= -2\delta_1^{A(B)} - 10\delta_2^{A(B)}, \\ \Delta_3^{A(B)} &= +2\delta_1^{A(B)} + 2\delta_2^{A(B)}\end{aligned}\quad (37)$$

Employing Eqs. (31)–(34) one obtains:

$$D_A = 4\varphi_{AB} - 4\varphi_{AA} + 12[-\alpha^A\varphi_{AA}(1 + 3\beta^A) + \alpha^B\varphi_{AB}(1 + 3\beta^B)] \quad (38)$$

$$D_B = 4\varphi_{AB} - 4\varphi_{BB} + 12[-\alpha^B\varphi_{BB}(1 + 3\beta^B) + \alpha^A\varphi_{AB}(1 + 3\beta^A)] \quad (39)$$

$$\begin{aligned}D_A + D_B &= 8\varphi_{AB} - 4\varphi_{AA} - 4\varphi_{BB} - 12[\alpha^A(1 + 3\beta^A)(\varphi_{AA} - \varphi_{AB}) \\ &\quad - \alpha^B(1 + 3\beta^B)(\varphi_{AB} - \varphi_{BB})]\end{aligned}\quad (40)$$

The parabolic relationship between splittings, Eq. (30), significantly simplifies Eq. (8) to yield:

$$\begin{aligned}F &= x_A F_{AAAA}^A + (1 - x_A) F_{BBBB}^B + c_4 x_A^4 + c_3 x_A^3 + c_2 x_A^2 + c_1 x_A \\ &\quad + \frac{1}{2} NkT [u_1 \ln u_1 + (1 - u_1) \ln(1 - u_1) + u_2 \ln u_2 + (1 - u_2) \ln(1 - u_2)]\end{aligned}\quad (41)$$

in which:

$$\begin{aligned}c_4 &= -8(\delta_2^A + \delta_2^B)(1 - s^4) \\ c_3 &= 6(\delta_1^A - \delta_1^B + 5(\delta_2^A - \delta_2^B))(1 - s^2) + 32\delta_2^B \\ c_2 &= (-6(\delta_1^A - \delta_1^B) - 22(\delta_2^A - \delta_2^B) - D_B - D_A)(1 - s^2) + (14\delta_2^B + 6\delta_1^B)(1 + s^2) - 16\delta_2^B \\ c_1 &= D_A + D_B - 6\delta_1^B - 14\delta_2^B\end{aligned}\quad (41a)$$

The coefficient of the highest order term depends solely on  $\delta_2^{A(B)}$ , hence (according to Eqs. (33) and (34)) on quaternary interactions alone. These parameters however enter lower order terms and therefore in order to get zero contribution of ternary interactions both  $\delta_1$  and  $\delta_2$  must be zero. This is a reasonable condition because it is difficult to imagine a situation when interactions of the 4-th order exist but ternary interactions are absent. Parameters  $\delta$  can be considered as *rationalised asymmetries* of splittings.

Similarly to the case of primary effects we must distinguish the cases of compensation ( $\beta^A = \beta^B$ ) and anti-compensation ( $\beta^A = -\beta^B$ ) of quaternary interactions (Eqs. (33) and (34)). In the first instance the highest order term disappears, whereas in the second case it is maximal. The magnitude of the total relative effect of quaternary interactions can hardly be larger than that of ternary interactions; taking into account the ratio of primary and secondary effects *per* tetrahedron (12:36) one can assume  $|\beta| \leq |\frac{1}{3}\alpha|$ . To a first approximation ternary and quaternary interactions can thus be characterised by one parameter  $\alpha^A$  together with regularisation bounds:  $\alpha^B = \pm\alpha^A$ ,  $\beta^A = \pm\frac{1}{3}\alpha^A$ ,  $\beta^B = \pm\beta^A$ .

A wide spectrum of non-ideality parameters can be obtained from various combinations of  $\alpha^A$ ,  $\Delta\varphi = \varphi_{AA} - \varphi_{BB}$  and deviations ( $\kappa$ ) from the *Berthelot* rule, (see Tables 5 and 6). When  $\alpha^B \neq \alpha^A$  but  $\beta^B = \beta^A$  secondary effects are compen-

**Table 5.** Non-ideality parameters computed for a system with anti-compensated primary and compensated secondary effects:  $\alpha^A = -\alpha^B = 3\beta^A$ ,  $\beta^B = \beta^A$ ,  $\varphi_{BB} = -12$  kJ/mol,  $\Delta\varphi = \varphi_{AA} - \varphi_{BB}$ ; due to compensation  $\delta_2^{A(B)} = 0$

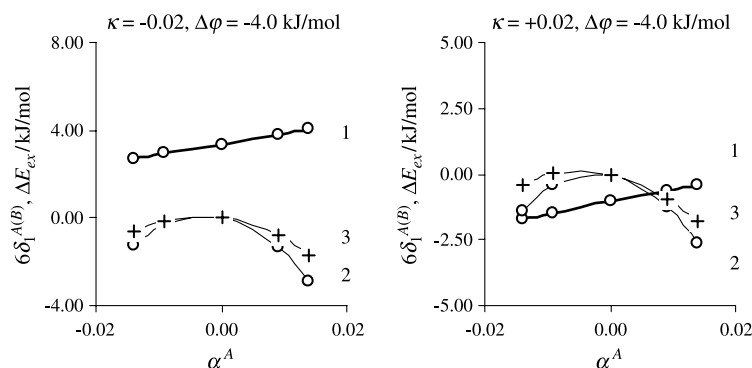
$\Delta\varphi$ kJ/mol	$\alpha$	$\frac{\Delta E_{ex}}{\text{kJ/mol}}$	$\frac{6\delta_1^A}{\text{kJ/mol}}$	$\frac{6\delta_1^B}{\text{kJ/mol}}$	$\frac{\Delta E_{ex}}{\text{kJ/mol}}$	$\frac{6\delta_1^A}{\text{kJ/mol}}$	$\frac{6\delta_1^B}{\text{kJ/mol}}$	$\frac{\Delta E_{ex}}{\text{kJ/mol}}$	$\frac{6\delta_1^A}{\text{kJ/mol}}$	$\frac{6\delta_1^B}{\text{kJ/mol}}$
		$\kappa = -0.03$			$\kappa = +0.03$			$\kappa = 0.0$		
-4.0	0.04	7.316	-3.636	-2.047	0.665	-2.455	-3.228	3.990	-3.046	-2.638
	0.000	4.474	0.000	0.000	-2.177	0.000	0.000	1.149	0.000	0.000
	-0.040	3.476	1.278	0.719	-3.175	0.863	1.134	0.150	1.070	0.927
0.0	0.040	2.880	-0.511	0.511	-2.880	0.511	-0.511	0.000	0.000	0.000
	0.000	2.880	0.000	0.000	-2.880	0.000	0.000	0.000	0.000	0.000
	-0.040	2.880	0.180	-0.180	-2.880	-0.180	0.180	0.000	0.000	0.000
4.0	0.040	1.126	2.137	3.546	-3.577	2.972	2.711	-1.225	2.555	3.129
	0.000	3.968	0.000	0.000	-0.735	0.000	0.000	1.616	0.000	0.000
	-0.040	4.966	-0.751	-1.246	0.263	-1.044	-0.953	2.615	-0.898	-1.099

**Table 6.** Non-ideality parameters computed for a system with anti-compensated primary and secondary effects:  $\alpha^A = -\alpha^B$ ,  $\beta^B = -\beta^A = \frac{1}{3}\alpha^A$ ,  $\varphi_{BB} = -12$  kJ/mol,  $\Delta\varphi = \varphi_{AA} - \varphi_{BB}$

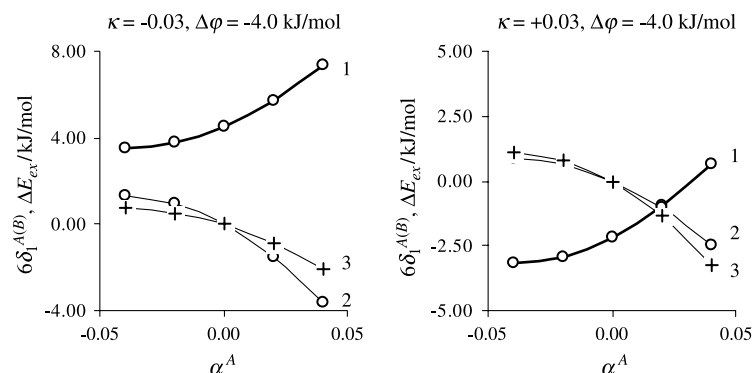
$\Delta\varphi$	$\alpha$	$\frac{\Delta E_{ex}}{\text{kJ/mol}}$	$\frac{6\delta_1^A}{\text{kJ/mol}}$	$\frac{6\delta_1^B}{\text{kJ/mol}}$	$\frac{2\delta_2^A}{\text{kJ/mol}}$	$\frac{2\delta_2^B}{\text{kJ/mol}}$	$\frac{\Delta E_{ex}}{\text{kJ/mol}}$	$\frac{6\delta_1^A}{\text{kJ/mol}}$	$\frac{6\delta_1^B}{\text{kJ/mol}}$	$\frac{2\delta_2^A}{\text{kJ/mol}}$	$\frac{2\delta_2^B}{\text{kJ/mol}}$
		$\kappa = -0.02, \beta^B = -\beta^A$					$\kappa = +0.02, \beta^B = -\beta^A$				
-4.0	0.014	4.062	-2.893	-1.707	0.046	-0.030	-0.404	-2.644	-1.831	0.035	-0.040
	0.000	3.366	0.000	0.000	0.000	0.000	-1.068	0.000	0.000	0.000	0.000
	-0.014	2.718	-1.266	-0.646	0.046	-0.030	-1.748	-1.390	-0.397	0.035	-0.040
0.0	0.014	1.934	-1.462	-1.301	0.005	0.005	-1.934	-1.247	-1.408	-0.005	-0.005
	0.000	1.920	0.000	0.000	0.000	0.000	-1.920	0.000	0.000	0.000	0.000
	-0.014	1.934	-1.301	-1.462	0.005	0.005	-1.934	-1.408	-1.247	-0.005	-0.005
4.0	0.014	2.534	-0.184	-0.820	-0.030	0.045	-0.623	-0.008	-0.907	-0.038	0.038
	0.000	3.184	0.000	0.000	0.000	0.000	0.049	0.000	0.000	0.000	0.000
	-0.014	3.878	-1.261	-2.431	-0.030	0.045	0.721	-1.348	-2.255	-0.038	0.038
		$\beta^B = \beta^A$									
-4.0	-0.014	2.807	0.677	0.441	0.000	0.000	-1.627	0.522	0.596	0.000	0.000
	0.000	3.366	0.000	0.000	0.000	0.000	-1.068	0.000	0.000	0.000	0.000
	0.014	4.1507	-0.9500	-0.6198	0.0000	0.0000	-0.283	-0.732	-0.837	0.000	0.000

sated and finite differences of second order are zero and hence  $\delta_2^{A(B)} = 0$ . However, secondary effects contribute towards  $\delta_1$  and  $\Delta E_{ex}$  making their dependencies on  $\alpha$  parabolic (Fig. 6) and not linear as when  $\beta = 0$  (Fig. 4).

A similar situation arises when primary effects are compensated ( $\alpha^A = \alpha^B$ ) but secondary are not ( $\beta^B = -\beta^A$ ). Complete compensation,  $\alpha^A = \alpha^B$  and  $\beta^A = \beta^B$ , yields the approximation of binary interactions ( $\delta_1 = 0$ ,  $\delta_2 = 0$ ). Non-zero  $\alpha$  and  $\beta$  in such a case contribute insignificantly towards  $\Delta E_{ex}$ .



**Fig. 6.** Dependencies of non-ideality parameters on relative many-centre effects ( $\alpha^A$ ,  $\alpha^B = -\alpha^A$ ,  $\Delta\varphi = \varphi_{AA} - \varphi_{BB}$ ,  $\kappa$  is the deviation from *Berthelot's* rule); secondary effects are non-zero ( $\beta^A = \frac{1}{3}\alpha^A$ ) but compensated ( $\beta^B = \beta^A$ ) leading to  $\delta_2^{A(B)} = 0$ ; thick lines (1) refer to  $\Delta E_{ex}$ , thin lines refer to  $\delta_1^A$  (2) and  $\delta_1^B$  (3)

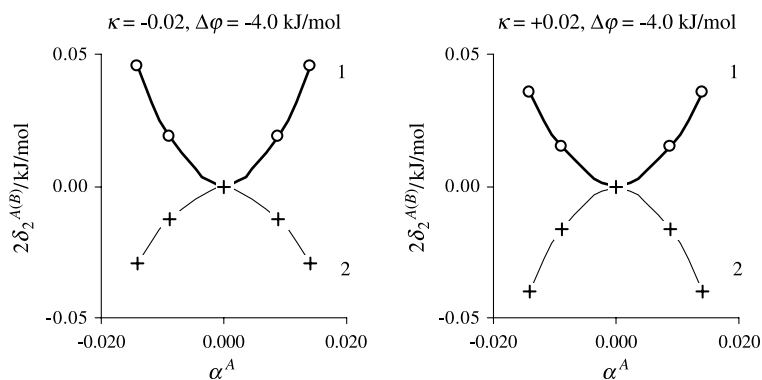


**Fig. 7.** Dependencies of non-ideality parameters on relative effects of the third bodies ( $\alpha^A$ ); both primary and secondary effects are anti-compensated ( $\alpha^B = -\alpha^A$ ,  $\beta^B = -\beta^A = -\frac{1}{3}\alpha^A$ ); thick lines (1) refer to  $\Delta E_{ex}$ , thin lines refer to  $\delta_1^A$  (2) and  $\delta_1^B$  (3)

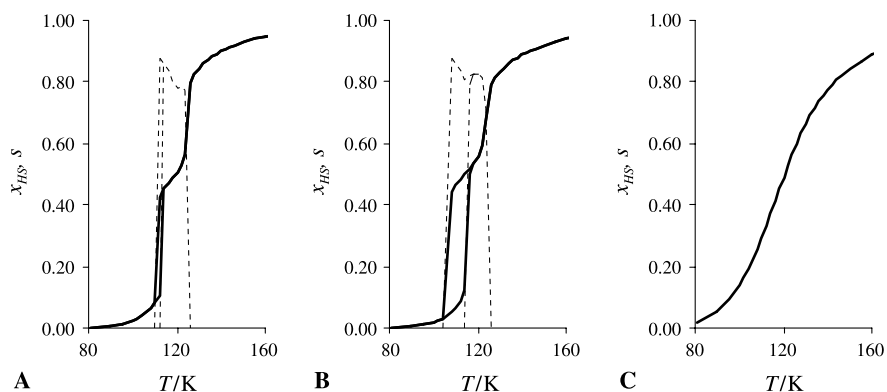
Non-zero second order differences (quadratic variations of splittings) appear when *both primary and secondary* effects are anti-compensated (Table 6) giving rise to considerable asymmetries. Corresponding dependencies of  $\delta_1$  and  $\delta_2$  on  $\alpha$  are shown in Figs. 7 and 8.

Arbitrary zeroing of  $\delta_2$  visibly changes the shape of a transition curve (compare Fig. 9A and B) but does not alter the nature of the transition (two-step spin crossover with sharp steps). Much larger effects are produced when zero values of  $\delta_2$  are achieved by the compensation  $\beta^A = \beta^B$ : this affects not only  $\delta_2$  but also changes  $\Delta E_{ex}$  and  $\delta_1$ .

The last three rows in Table 6 show non-ideality parameters computed similarly to the first three rows but with compensated  $\beta$ . The values of  $\Delta E_{ex}$ , and  $\delta_1^{A(B)}$  in these two cases are considerably different (especially at  $\kappa = +0.02$ ). This leads to a striking difference in the shape of transition curves shown in Fig. 9A and C. The model of ternary interactions thus implicitly represents a considerable part of the effects of quaternary interactions.



**Fig. 8.** Dependencies of second-order non-ideality parameters  $\delta_2^A$  (1) and  $\delta_2^B$  (2) on relative effects of the third bodies ( $\alpha^A$ ); both primary and secondary effects are anti-compensated ( $\alpha^B = -\alpha^A$ ,  $\beta^B = -\beta^A = -\frac{1}{3}\alpha^A$ )



**Fig. 9.** Transition curves of a hypothetical system characterised by  $\Delta E^0 = 7$  kJ/mol,  $T_{1/2} = 120$  K; graph A corresponds to  $\Delta E_{ex} = -0.404$  kJ/mol,  $6\delta_1^A = -2.644$  kJ/mol,  $6\delta_1^B = -1.831$  kJ/mol,  $2\delta_2^A = 0.035$  kJ/mol, and  $2\delta_2^B = -0.04$  kJ/mol (first row of Table 6 for  $\kappa = +0.02$ ); graph B was computed for the same set of parameters save  $\delta_2^A = \delta_2^B = 0$ ; graph C was obtained with  $\Delta E_{ex} = -0.283$  kJ/mol,  $\delta_1^A = -0.732$  kJ/mol,  $\delta_1^B = -0.837$  kJ/mol, and  $\delta_2^A = \delta_2^B = 0$  arising from compensation of secondary effects (last row in Table 6)

A similar analysis can be performed for the case of the cubic variation of splittings that arises from 5-centre interactions considered as tertiary effects  $\varepsilon_{ij}^{m(l(k))}$  (see Appendix A2). The equation for free energy contains an expansion over the powers of  $x_A$  up to the 5-th power

$$F = x_A F_{AAAA}^A + (1 - x_A) F_{BBBB}^B + c_5 x_A^5 + c_4 x_A^4 + c_3 x_A^3 + c_2 x_A^2 + c_1 x_A + \frac{1}{2} NkT [u_1 \ln u_1 + (1 - u_1) \ln(1 - u_1) + u_2 \ln u_2 + (1 - u_2) \ln(1 - u_2)] \quad (42)$$

in which:

$$c_5 = (1 - s^2)(1 + 3s^2)(+6\delta_3^A - 6\delta_3^B)$$

$$c_4 = -8\delta_2^A - 48\delta_3^A - 8\delta_2^B - 18\delta_3^B + 36\delta_3^B s^2 + (8\delta_2^A + 48\delta_3^A + 8\delta_2^B + 30\delta_3^B) s^4$$



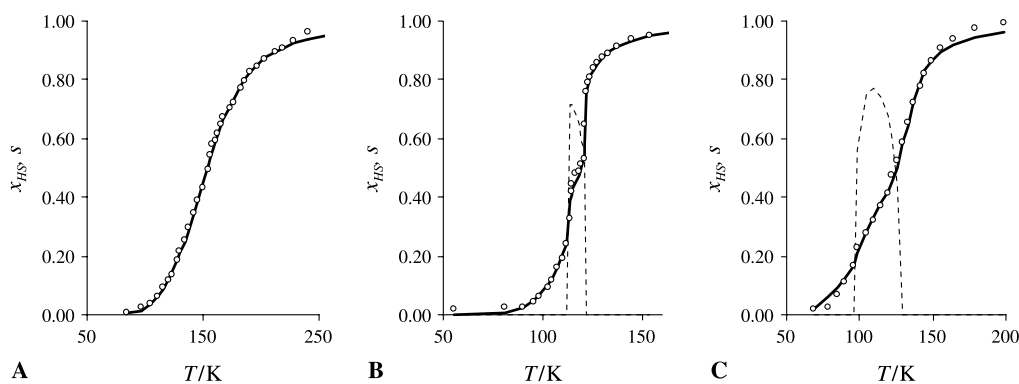
$$\begin{aligned}
 c_3 &= 6\delta_1^A + 30\delta_2^A + 114\delta_3^A - 6\delta_1^B + 2\delta_2^B + 18\delta_3^B \\
 &\quad + (6\delta_1^B + 30\delta_2^B + 78\delta_3^B - 6\delta_1^A - 30\delta_2^A - 114\delta_3^A)s^2 \\
 c_2 &= 12\delta_1^B + 20\delta_2^B + 42\delta_3^B - 6\delta_1^A - 22\delta_2^A - 72\delta_3^A - D_A - D_B \\
 &\quad + (6\delta_1^A + 22\delta_2^A + 72\delta_3^A - 8\delta_2^B - 30\delta_3^B + D_A + D_B)s^2 \\
 c_1 &= -6\delta_1^B - 14\delta_2^B - 36\delta_3^B + D_A + D_B
 \end{aligned}
 \tag{42a}$$

Five-centre interactions are formally characterised by the rationalised asymmetries of the third order ( $\delta_3^{A(B)}$ ). The latter can be computed for known binary potentials, deviations from *Berthelot's* rule, and the relative primary, secondary, and tertiary effects ( $\alpha$ ,  $\beta$ , and  $\gamma$ ). However the effect of taking into account 5-centre interactions on the shape of spin crossover transition curves is smaller than that of the quaternary interactions. In the regressional analysis of experimental transition curves it is therefore sufficient to limit the expansion of free energy to the fourth power of  $x_A$ .

### Fitting of Experimental Data

Recently a systematic study of spin crossover in a series of solvates  $[\text{Fe}(2\text{-pic})_3]\text{Cl}_2\text{solv}$  ( $2\text{-pic} = 2\text{-picolylamine}$ ,  $\text{solv} = \text{MeOH}$ ,  $\text{EtOH}$ , allyl alcohol,  $n\text{-PrOH}$ ,  $iso\text{-PrOH}$ ,  $t\text{-BuOH}$ ) has been reported (Fig. 10) [22]. Variation of solvating molecule causes a spectacular change from a gradual transition in the  $\text{MeOH}$  solvate to a sharp two-step spin crossover in the  $\text{EtOH}$  solvate, poorly defined two-step spin crossover in the allyl alcohol solvate, complicated curve with several steps (apparently arising from minor structural transitions) in the  $iso\text{-PrOH}$  solvate, and no transition at all (complexes remaining high-spin down to 4 K) in the  $n\text{-PrOH}$  and  $t\text{-BuOH}$  solvates. Nevertheless the crystal structures of all these compounds at 200 K have been found to be astonishingly similar.

Two major factors control the variations of spin-crossover behaviour in this series, first of all the ligand-field strength. In the solid state it is not a property of a ligand molecule but depends strongly on the metal-to-ligand distance (as has



**Fig. 10.** Experimental transition curves of spin crossover in  $[\text{Fe}(2\text{-pic})_3]\text{Cl}_2\text{solv}$  [22] ( $\text{solv} = \text{MeOH}$  (A),  $\text{EtOH}$  (B), and allyl alcohol (C)) approximated by the model of ternary interactions; dashed lines represent the degree of order

been recently emphasized by A. Hauser [23]) controlled not so much by the metal-ligand interaction as by details of the crystal structure reflecting the balance of all forces acting between all particles constituting a crystal. Small changes in the geometry considerably affect the effective ligand-field strength ( $10Dq$  being proportional to  $r^{-6}$  or  $r^{-5}$  [23]). Therefore it is not entirely unexpected that solvent molecules, although residing in the second coordination sphere, change the magnetic behaviour.

Another factor is the variation of binary and many-centre interactions between complexes in equilibrium. Solvent molecules being on the line of interaction of metal centres affect, to a considerable extent, both repulsive and attractive parts of binary potentials. They also participate in hydrogen bonding and this changes parameters of binary interactions between neighbouring molecules. This brings about a variation of the contribution of many-centre molecular interactions towards the lattice energy, and hence non-ideality terms in the derived equations. Fitting the transition curves of *MeOH*, *EtOH*, and allyl alcohol solvates according to the derived equations allowed us to determine the extent of this variation. We did not analyse the curve of the *iso-PrOH* solvate because according to Ref. [22] this compound undergoes a structural transition that affects the transition curve.

The regression of these transition curves easily converges when analysed in terms of rational asymmetries ( $\delta_i^{A(B)}$ ),  $\Delta E_{ex}$ , and  $T_{1/2} = \Delta E^0 / \Delta S^0$  (the values of  $\Delta E^0$  were fixed according to the calorimetric data). Direct fitting in terms of  $\varphi_{AA}$ ,  $\alpha^A$ ,  $\beta^A$ ,  $\gamma^A$  (with regularisation of conditions corresponding to anti-compensation),  $\kappa$ , and  $T_{1/2}$  was also successful in several cases, however, in general, it required a very precise initial guess and did not converge smoothly. We performed therefore parameterisation in terms of  $\Delta E_{ex}$  and rationalised asymmetries whereas the values of  $\alpha^A$ ,  $\beta^A$ ,  $\gamma^A$ ,  $\varphi_{AA}$ , and  $\kappa$  have been obtained from estimates of  $\delta_1^{A(B)}$ ,  $\delta_2^{A(B)}$ ,  $\delta_3^{A(B)}$ , and  $\Delta E_{ex}$  employing a simple optimisation procedure according to the relationships presented in the previous section and carried out in Microsoft Excel<sup>TM</sup> worksheets.

**Table 7.** Estimates of parameters of Eqs. (23) and (41) obtained by regression of experimental transition curves [22] of spin crossover in  $[\text{Fe}(2\text{-pic})_3]\text{Cl}_2\text{solv}$  ( $\text{solv} = \text{MeOH}, \text{EtOH}, \text{allyl-OH}, T_{1/2} = \Delta E^0 / \Delta S^0$ )

	$100\sigma_{yx}$	$\frac{\Delta E^0}{\text{kJ/mol}}$	$\frac{T_{1/2}}{\text{K}}$	$\frac{\Delta E_{ex}}{\text{kJ/mol}}$	$\frac{6\delta_1^A}{\text{kJ/mol}}$	$\frac{6\delta_1^B}{\text{kJ/mol}}$	$\frac{2\delta_2^A}{\text{kJ/mol}}$	$\frac{6\delta_2^B}{\text{kJ/mol}}$
The model of binary interactions								
1 <i>MeOH</i>	1.33	8.8	$152.9 \pm 0.3$	$0.29 \pm 0.04$	0	0	0	0
The model of ternary interactions								
2 <i>MeOH</i>	1.12	8.8	$152.1 \pm 0.3$	$0.310 \pm 0.04$	$0.19 \pm 0.05$	-0.19	0	0
3 <i>EtOH</i>	2.14	6.14	$115.3 \pm 0.2$	$-0.32 \pm 0.01$	$-1.65 \pm 0.05$	$-2.28 \pm 0.01$	0	0
4 Allyl-OH	1.97	6.14	$116.7 \pm 0.5$	$-0.89 \pm 0.04$	$-0.47 \pm 0.12$	$-2.22 \pm 0.06$	0	0
The model of quaternary interactions								
5 <i>EtOH</i>	2.04	6.14	$115.6 \pm 0.3$	$-0.30 \pm 0.03$	$-1.61 \pm 0.29$	$-2.36 \pm 0.01$	$-0.007 \pm 0.038$	$0.012 \pm 0.004$
6 Allyl-OH	1.69	6.14	$117.0 \pm 0.7$	$-0.09 \pm 0.13$	$-4.09 \pm 0.45$	$-0.02 \pm 0.34$	$0.55 \pm 0.06$	$-0.239 \pm 0.026$

A smooth curve of nearly gradual transition in the *MeOH* derivative cannot yield a large number of non-ideality parameters: it is practically adequately ( $100\sigma_{yx}=1.32$ , Table 7) described by the model of binary interactions with small positive excess energy  $\Delta E_{ex}=+0.29\pm 0.04$  kJ/mol. This parameter can arise from a number of combinations of microscopic parameters, *e.g.* zero or compensated  $\alpha$ ,  $\beta$ , and  $\gamma$  along with zero or non-zero  $\kappa$ . For example it can be assumed that  $\varphi_{AA}-\varphi_{BB}=-1.967$  kJ/mol whereas  $\varphi_{AB}$  follows the *Berthelot* rule ( $\kappa=0$ ), many-body interactions being zero. Another possibility is that  $\varphi_{AA}-\varphi_{BB}=0$  but HS-LS pairs are destabilised ( $\kappa=-0.031$ ). Only a slightly better description is obtained within the model of ternary interactions using regularisation bounds:  $\delta_1^B=-\delta_1^A$  (second row in Table 7, Fig. 11A). These estimates can be explained as arising from destabilisation of HS-LS pairs ( $\kappa=-0.0032$ ) and considerable anti-compensated primary effects  $\alpha^A=-0.2$ ,  $\alpha^B=+0.2$  at zero difference of binary potentials ( $\varphi_{AA}-\varphi_{BB}=0$ ).

The curve of the *EtOH* solvate has been adequately described within the model of ternary interactions. Employing a fixed value of the enthalpy of transition  $\Delta E^0=6.14$  kJ/mol (calorimetric data [24]) well defined estimates of  $\Delta E_{ex}$ ,  $\delta_1^A$ , and  $\delta_1^B$  have been obtained (row 3 in Table 7; Fig. 10B). These estimates can be represented as arising from positive anti-compensated  $\alpha^A=0.046$ ,  $\alpha^B=-0.046$ , stabilisation of HS-LS pairs ( $\kappa=+0.029$ ), and considerable difference of AA and BB potentials ( $\varphi_{AA}-\varphi_{BB}=-3.51$  kJ/mol). The contribution of ternary interactions thus amounts to *ca.*  $\alpha=0.04$  of the contribution of binary interactions. This is in the agreement with the established views on the relative role of binary and many-body molecular interactions [25]. A slightly better description can be obtained within the model of quaternary interactions (non-zero  $\delta_2^{A(B)}$ , Table 7, row 5). Estimates of  $\Delta E_{ex}$ ,  $\delta_1^A$ , and  $\delta_1^B$  are not much different from those obtained with zero  $\delta_2^{A(B)}$ . Corresponding  $\alpha^A$  are smaller than in the model of ternary interactions whereas negative  $\Delta\varphi$  are larger ( $\alpha^A=+0.036$ ,  $\alpha^B=-0.036$ ;  $\beta^A=-0.0003$ ,  $\beta^B=+0.0003$ ;  $\kappa=0.0378$ ;  $\varphi_{AA}-\varphi_{BB}=-5.234$ ).

The curve of the allyl alcohol solvate can be described employing models of ternary and quaternary interactions (rows 4 and 6 in Table 7). In the absence of calorimetric data on this compound it was assumed that  $\Delta E^0=6.14$  kJ/mol as in the case of *EtOH* solvate. Within the model of ternary interactions (Table 7, row 4, Fig. 10C) obtained estimates correspond to the stabilisation of HS-LS pairs and small negative difference of binary potentials ( $\alpha^A=+0.13$ ,  $\alpha^B=-0.13$ ,  $\kappa=+0.023$ ,  $\varphi_{AA}-\varphi_{BB}=-0.86$  kJ/mol). The model of quaternary interactions yields a slightly better accuracy (row 6 of Table 7) and estimates that imply a destabilisation of HS-LS pairs and a large difference of AA and BB potentials ( $\alpha^A=-0.1$ ,  $\alpha^B=+0.1$ ;  $\beta^A=-0.0037$ ,  $\beta^B=+0.0037$ ;  $\kappa=-0.045$ ;  $\varphi_{AA}-\varphi_{BB}=-7.2$  kJ/mol). Microscopic interpretations of estimates obtained in the models of ternary and quaternary interactions are thus different; however errors of regression are too close for a reliable decision concerning the most probable model. According to *Occam's* principle the model of ternary interactions is preferable.

Indeed the model of ternary interactions seems to be the most versatile: it describes the whole set of analysed data. Estimates of  $\alpha^A$  obtained within this model regularly increase in the series of *MeOH*, *EtOH*, and allyl alcohol solvates. The stabilisation of HS-LS pairs ( $\kappa$ ) and the difference of AA and BB

potential vary unsystematically however within a feasible range. Probably the choice of the fixed value of the enthalpy of transition for the allyl-OH solvate was not correct.

### Comparison with the Formalism Based on *Landau* Theory

*Landau* theory allows one to derive phenomenological formalisms describing processes involving phase transitions without having recourse to molecular models. Being applied to the solid-state spin crossover this theory yielded [13] an expression for free energy similar but not identical to that of the model of ternary interactions [15]. The model based on *Landau* theory predicts the general features of experimental two-step transition curves – however it fails to produce a quantitative parameterisation of experimental data whereas the essentially microscopic model of ternary interactions [15] provides for an adequate description yielding well-defined estimates of parameters. It is therefore of interest to compare these two formalisms.

The models employ different variables: the model of many-body interactions uses the composition ( $x_A$ ) and the degree of order ( $s$ ) whereas the model based on *Landau* theory employs order parameters  $x$  and  $y$  connected with the composition and the degree of order as:

$$x = \frac{N_{HS} - N_{LS}}{N_{HS} + N_{LS}} = x_B - x_A = 1 - 2x_A, \quad \text{hence:} \quad x_A = \frac{1}{2}(1 - x) \quad (43)$$

$$y = \frac{N_{HS}^A - N_{HS}^B}{N_{HS} + N_{LS}} = X_B - X_A = sx_A \quad (44)$$

The free energy of the model of ternary interactions (Eq. (23)) can be written (omitting for simplicity the mixing entropy) as:

$$F = A_0 + A_1x_A + A_{20}x_A^2 + A_3x_A^3 + A_{22}s^2x_A^2 - A_3s^2x_A^3 \quad (45)$$

in which:

$$\begin{aligned} A_0 &= F_{BBBB}^B, \quad A_1 = -6\delta^B + D_A + D_B - \Delta F^0, \\ A_{20} &= -6\delta^A + 12\delta^B - D_B - D_A, \quad A_{22} = 6\delta^A + D_A + D_B, \quad A_3 = 6\delta^A - 6\delta^B \end{aligned} \quad (46)$$

By substituting  $x_A$  and  $s$  according to Eqs. (43) and (44) one obtains:

$$F = \alpha_0 + \alpha_1x + \alpha_2x^2 + \alpha_3x^3 + \beta_2y^2 + \lambda_{21}y^2x \quad (47)$$

in which:

$$\begin{aligned} \alpha_0 &= A_0 + \frac{1}{2}A_1 + \frac{1}{4}A_{20} + \frac{1}{8}A_3, \quad \alpha_1 = -\frac{1}{2}A_1 - \frac{1}{2}A_{20} - \frac{3}{8}A_3, \quad \alpha_2 = \frac{1}{4}A_{20} + \frac{3}{8}A_3, \\ \alpha_3 &= -\frac{1}{8}A_3, \quad \beta_2 = A_{22} - \frac{1}{2}A_3, \quad \lambda_{21} = \frac{1}{2}A_3y^2 \end{aligned} \quad (48)$$

Expressing coefficients  $A_{ij}$  in terms of  $\delta_1^{A(B)}$  and  $D_{A(B)}$  according to Eq. (46) yields:

$$\begin{aligned} \alpha_0 &= F_{BBBB}^B + \frac{1}{4}(D_A + D_B) - \frac{1}{2}\Delta F^0 - \frac{3}{4}(\delta_1^A + \delta_1^B), \quad \alpha_1 = \frac{3}{4}(\delta_1^A - \delta_1^B) + \frac{1}{2}\Delta F^0 \\ \alpha_2 &= \frac{3}{4}(\delta_1^A + \delta_1^B) - \frac{1}{4}(D_B + D_A), \quad \alpha_3 = -\frac{3}{4}(6\delta_1^A - \delta_1^B) \\ \beta_2 &= D_A + D_B + 3(\delta_1^A + \delta_1^B), \quad \lambda_{21} = 3(\delta_1^A - \delta_1^B) \end{aligned} \quad (49)$$

Rationalised asymmetries (and hence the coefficients in Eq. (47)) can be represented *via* many-centre effects and molecular potentials as described earlier, *i.e.* interpreted microscopically. Compared to the free energy derived from *Landau* theory [13]:

$$F = \alpha_0 + \alpha_2 x^2 + \alpha_4 x^4 + \beta_2 y^2 + \beta_4 y^4 + \lambda_{21} y^2 x + \lambda_{22} y^2 x^2 \quad (50)$$

Equation (47) additionally contains linear and cubic terms in  $x$  but lacks the fourth-order terms in  $x$  and  $y$  as well as the bi-quadratic coupling term  $\lambda_{22} y^2 x^2$ .

Higher order terms can be introduced by considering higher order molecular interactions. For example the model of quaternary interactions (Eq. (41)) yields:

$$F = \alpha_0 + \alpha_1 x + \alpha_2 x^2 + \alpha_3 x^3 + \alpha_4 x^4 + \beta_2 y^2 + \beta_4 y^4 + \lambda_{21} y^2 x \quad (51)$$

in which:

$$\alpha_0 = F_B + \frac{1}{4}(D_A + D_B) - \frac{1}{2}\Delta F^0 - \frac{3}{4}(\delta_1^A + \delta_1^B) - \frac{9}{4}(\delta_2^A + \delta_2^B) \quad (52)$$

$$\alpha_1 = \frac{3}{4}(\delta_1^A - \delta_1^B) + \frac{7}{4}(\delta_2^A - \delta_2^B) + \frac{1}{2}\Delta F^0 \quad (53)$$

$$\alpha_2 = \frac{3}{4}(\delta_1^A + \delta_1^B) + \frac{11}{4}(\delta_2^A + \delta_2^B) - \frac{1}{4}(D_A + D_B) \quad (54)$$

$$\alpha_3 = -\frac{3}{4}(\delta_1^A - \delta_1^B) - \frac{7}{4}(\delta_2^A - \delta_2^B) \quad (55)$$

$$\alpha_4 = -\frac{1}{2}(\delta_2^A + \delta_2^B) \quad (56)$$

$$\beta_2 = +3(\delta_1^A + \delta_1^B) + 7(\delta_2^A + \delta_2^B) + D_A + D_B \quad (57)$$

$$\beta_4 = 8(\delta_2^A + \delta_2^B) + 39(\delta_3^A + \delta_3^B) \quad (58)$$

$$\lambda_{21} = 3(\delta_1^A - \delta_1^B) + 15(\delta_2^A - \delta_2^B) \quad (59)$$

Taking into account quaternary interactions thus gives rise to the fourth-order term in  $x$ . However it does not yield the bi-quadratic coupling term. An actual microscopic model of molecular interactions thus defines the rules of introducing new terms into a polynomial expansion of free energy.

The bi-quadratic coupling term appears when 5-centre interactions are taken into account. When free energy (Eq. (42)) is written employing variables  $x$  and  $y$ , it contains all terms present in the formal expansion of the model based on *Landau* theory [13] as well as additional terms with odd powers of  $x$  including two higher-order coupling terms:

$$F = \alpha_0 + \alpha_1 x + \alpha_2 x^2 + \alpha_3 x^3 + \alpha_4 x^4 + \alpha_5 x^5 + \beta_2 y^2 + \beta_4 y^4 + \lambda_{21} y^2 x + \lambda_{22} y^2 x^2 + \lambda_{32} y^2 x^3 + \lambda_{41} y^4 x \quad (60)$$

in which:

$$\alpha_0 = F_B + \frac{1}{4}(D_A + D_B) - \frac{1}{2}\Delta F^0 - \frac{3}{4}(\delta_1^A + \delta_1^B) - \frac{9}{4}(\delta_2^A + \delta_2^B) - \frac{105}{16}(\delta_3^A + \delta_3^B) \quad (61)$$

$$\alpha_1 = \frac{3}{4}(\delta_1^A - \delta_1^B) + \frac{7}{4}(\delta_2^A - \delta_2^B) + \frac{69}{16}(\delta_3^A - \delta_3^B) + \frac{1}{2}\Delta F^0 \quad (62)$$

$$\alpha_2 = \frac{3}{4}(\delta_1^A + \delta_1^B) + \frac{11}{4}(\delta_2^A + \delta_2^B) + \frac{69}{8}(\delta_3^A + \delta_3^B) - \frac{1}{4}(D_A + D_B) \quad (63)$$

$$\alpha_3 = -\frac{3}{4}(\delta_1^A - \delta_1^B) - \frac{7}{4}(\delta_2^A - \delta_2^B) - \frac{33}{8}(\delta_3^A - \delta_3^B) \quad (64)$$

$$\alpha_4 = -\frac{1}{2}(\delta_2^A + \delta_2^B) - \frac{33}{16}(\delta_3^A + \delta_3^B) \quad (65)$$

$$\alpha_5 = -\frac{3}{16}(\delta_3^A - \delta_3^B) \quad (66)$$

$$\beta_2 = 3(\delta_1^A + \delta_1^B) + 7(\delta_2^A + \delta_2^B) + 15(\delta_3^A + \delta_3^B) + \frac{3}{2}(\delta_3^A + \delta_3^B) + D_A + D_B \quad (67)$$

$$\beta_4 = 8(\delta_2^A + \delta_2^B) + 39(\delta_3^A + \delta_3^B) \quad (68)$$

$$\lambda_{21} = 3(\delta_1^A - \delta_1^B) + 15(\delta_2^A - \delta_2^B) + \frac{105}{2}(\delta_3^A - \delta_3^B) \quad (69)$$

$$\lambda_{22} = \frac{18}{4}(\delta_3^A + \delta_3^B) \quad (70)$$

$$\lambda_{23} = -\frac{3}{2}(\delta_3^A - \delta_3^B) \quad (71)$$

$$\lambda_{41} = 9(\delta_3^A - \delta_3^B) \quad (72)$$

This means that increasing the number of terms reflects taking into account higher order interactions. However new terms appear in a certain order defined by the actual model of interactions.

Odd power terms that distinguish the microscopic model developed above are vital for adequate description of ‘difficult’ two-step spin crossover transition curves [19], such as that of  $[\text{Fe}(2\text{-pic})_3]\text{Cl}_2\text{EtOH}$ , Fig. 10B. Odd power terms disappear when uneven rationalised asymmetries are pair-wise equal  $\delta_i^A = \delta_i^B$ . According to Eqs. (17)–(19) and (31) this is only possible when  $\varphi_{AB} = \frac{1}{2}(\varphi_{AA} + \varphi_{BB})$ , *i.e.* in a very special case in which contributions from binary interactions are compensated: both the excess energy and asymmetries arise from ternary interactions:

$$\delta_1^A = \delta_1^B = (\alpha^A - \alpha^B)(\varphi_{AA} - \varphi_{BB}) \quad (73)$$

$$D_B + D_A = -6(\alpha^A - \alpha^B)(\varphi_{AA} - \varphi_{BB}) = -6\delta_1^{A(B)} \quad (74)$$

Negative excess energy in this case is coupled to small positive  $\delta_1^{A(B)}$  (*i.e.* negative  $\Delta_1^{A(B)}$ ), which excludes the possibility of a two-step spin crossover. Microscopic interpretation of the formal expansion of free energy thus shows the importance of the odd-power terms.

Employing the order parameters  $x$  and  $y$  as main variables provides for certain mathematical simplicity: all coefficients of expansion are functions of differences and sums of rationalised asymmetries (see Eqs. (51)–(59) and (60)–(72)). However these variables are not independent and although the derivation of equations is more complicated when using  $x_A$  and  $s$ , the formulation of the condition of the minimum of free energy is considerably simplified for these independent and physically transparent variables.

## Conclusions

In this paper we have extended the earlier developed formalism describing non-ideality in binary molecular mixtures on the basis of the model of pseudo-independent molecules experiencing the effects from molecules in their nearest surrounding to systems with ordering and 5-centre molecular interactions.

Free energy of a molecule in this model is split into a quintet characterised by main splittings ( $D_A, D_B$ ) and asymmetries ( $\Delta_1^{A(B)}, \Delta_2^{A(B)}$ , and  $\Delta_3^{A(B)}$ ). The expression for free energy contains terms up to the 5-th order in the composition ( $x_A$ ) and 4-th order in the degree of order. This formalism is simplified in the cases of regular multiplets. Equidistant multiplets correspond to the model of binary interactions whereas multiplets with linearly varying splittings yield equations identical with those of the earlier developed model of ternary interactions. The models of quaternary and 5-centre interactions were obtained as special cases of splittings varying according to the polynomials of second and third order. These cases can be considered as representing different distributions of the density of states: higher order interactions correspond to progressively uneven distributions.

A new set of parameters (rationalised asymmetries of splittings  $\delta$ ) has been introduced that provided for the separation of the effects of interactions of different orders. These parameters have been microscopically interpreted employing a simple physical model representing ternary interactions as effects of the third molecule on a binary interaction; quaternary interactions were considered as effects of the fourth (external) molecule on a ternary interaction and so forth. This allowed us to represent free energy in terms of binary molecular potentials and relative efficiencies ( $\alpha, \beta$ , and  $\gamma$ ) of ternary, quaternary, and 5-centre interactions. By employing certain regularisation bounds, workable formalisms have been developed providing for regression analysis of experimental data.

Simulations have shown that the reduction of a chosen model to that of the lower order of interactions can be achieved at either zero ( $\alpha = 0, \beta = 0, \gamma = 0$ ) or compensated ( $\alpha^A = \alpha^B, \beta^A = \beta^B, \gamma^A = \gamma^B$ ) effects. It was found that higher order interactions *directly* contribute to terms formally arising from lower-order interactions. Both compensated and non-compensated coefficients  $\beta$  and  $\gamma$  considerably affect the terms arising from ternary interactions. At the same time higher order terms arising from non-compensated  $\beta$  and  $\gamma$  are not very large and although they change to some extent the shape of transition curve they do not change its nature. This fact explains the general applicability of the model of ternary interactions in the description of two-step transition curves. It was also found that many-centre interactions affect the excess energy (earlier considered as reflecting the contribution of binary interactions alone). Many-body interactions contribute several percent of the energy of binary interactions. They strongly affect, however, the shape of the transition curves of spin crossover.

The developed formalism has been compared to that based on the *Landau* theory [11]. *Landau* theory considers ordering as a structural transition whereas spin-crossover in systems without ordering can be treated as an iso-structural transition. In our model the degree of order ( $s$ ) is considered as a thermodynamic coordinate that indeed may have two values at a given temperature indicative of a phase transition. Furthermore, odd and even centres in the considered case of a diamond lattice form sublattices of a symmetry different from the initial one (hexagonal and diamond

lattices, respectively). Being preferentially filled by HS and LS molecules due to the strong hetero-molecular interaction these sublattices form a new crystal structure.

When expressed *via* the same variables these two formalisms yield similar, but not identical, expansions of free energy in powers of order parameters ( $x = 1 - 2x_A$  and  $y = sx_A$  used in Ref. [13]). The model described in the present paper yields even- and odd-power terms in  $x$ , the latter being avoided in the model based on *Landau* theory. According to microscopic interpretation, odd-power terms can indeed be zero (at  $\varphi_{AB} = \varphi_{AA} + \frac{1}{2}\varphi_{BB}$ ). However in such a case negative excess energies are coupled with negative asymmetries making the two-step spin cross-over impossible. *The odd-power terms are vital for obtaining adequate descriptions of a number of two-step transition curves.*

## Methods

Experimental data on spin crossover have been read from graphs in PDF files of published papers available on the Internet. Theoretical transition curves have been simulated by solving systems of equations derived from the condition of the minimum of free energy ( $\partial F/\partial x_A = 0$  and  $\partial F/\partial s = 0$ , see Refs. [15–17]). Non-linear regression has been performed employing a multipurpose regression program supplied with the monograph [26].

## Appendices

### *Primary Effects in Square-Planar Molecular Environment*

In this configuration one has to distinguish cis- and trans-effects also taking into account different probabilities of some molecular arrangements (Table A1). Irrespective of the actual magnitudes of cis- and trans-effects, finite differences of the first order are identical, *i.e.* differences of second and higher orders are zero.

Furthermore the ratio of cis- and trans-contributions is identical for all configurations (2:1, Table A1) allowing one to employ  $\varepsilon_{ij}^k$  as a single effective parameter similarly to that employed for the tetrahedral environment.

### *Five-Centre Interactions in the Tetrahedral Environment*

The cubic variation of splittings:

$$J_i^{A(B)} = J_1^{A(B)} + (i-1)\delta_1^{A(B)} + (i-1)^2\delta_2^{A(B)} + (i-1)^3\delta_3^{A(B)} \quad (\text{A1})$$

leads to the following asymmetries:

$$\Delta_i^{A(B)} = -10\delta_1^{A(B)} - 10\delta_2^{A(B)} - 40\delta_3^{A(B)} + 4i(\delta_1^{A(B)} - 2\delta_2^{A(B)} + 3\delta_3^{A(B)}) + 4i^2(\delta_2^{A(B)} - 3\delta_3^{A(B)}) + 4i^3\delta_3^{A(B)} \quad (\text{A2})$$

*i.e.:*

$$\Delta_1^{A(B)} = -6\delta_1^{A(B)} - 14\delta_2^{A(B)} - 36\delta_3^{A(B)} \quad (\text{A3})$$

$$\Delta_2^{A(B)} = -2\delta_1^{A(B)} - 10\delta_2^{A(B)} - 32\delta_3^{A(B)} \quad (\text{A4})$$

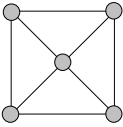
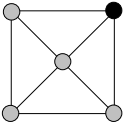
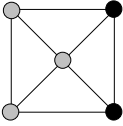
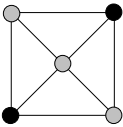
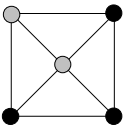
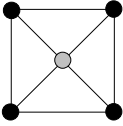
$$\Delta_3^{A(B)} = 2\delta_1^{A(B)} + 2\delta_2^{A(B)} - 4\delta_3^{A(B)} \quad (\text{A5})$$

The free energy (Eq. (8)) expressed in terms of  $\delta_i^{A(B)}$  contains a term proportional to  $x_A^5$  hence a contribution from 5-th order interactions:



$$\begin{aligned}
F = & x_A F_{AAAA}^A + (1-x_A) F_{BBBB}^B + (1-s^2)(1+3s^2)(+6\delta_3^A - 6\delta_3^B)x_A^5 \\
& + \left( \begin{array}{l} -8\delta_2^A - 48\delta_3^A - 8\delta_2^B - 18\delta_3^B \\ s^2(+36\delta_3^B) \\ s^4(+8\delta_2^A + 48\delta_3^A + 8\delta_2^B + 30\delta_3^B) \end{array} \right) x_A^4 + \left( \begin{array}{l} +6\delta_1^A + 30\delta_2^A + 114\delta_3^A - 6\delta_1^B + 2\delta_2^B + 18\delta_3^B \\ (-6\delta_1^A - 30\delta_2^A - 114\delta_3^A + 6\delta_1^B + 30\delta_2^B + 78\delta_3^B)s^2 \end{array} \right) x_A^3 \\
& + \left( \begin{array}{l} -6\delta_1^A - 22\delta_2^A - 72\delta_3^A + 12\delta_1^B + 20\delta_2^B + 42\delta_3^B - D_A - D_B \\ (+6\delta_1^A + 22\delta_2^A + 72\delta_3^A - 8\delta_2^B - 30\delta_3^B + D_A + D_B)s^2 \end{array} \right) x_A^2 \\
& + (-6\delta_1^B - 14\delta_2^B - 36\delta_3^B + D_A + D_B)x_A \\
& + \frac{1}{2}NkT[u_1 \ln u_1 + (1-u_1) \ln(1-u_1) + u_2 \ln u_2 + (1-u_2) \ln(1-u_2)]
\end{aligned} \tag{A6}$$

**Table A1.** Primary effects in a square-planar molecular environment

	$\epsilon_{AA}^{A_{cis}}$	$\epsilon_{AB}^{A_{cis}}$	$\epsilon_{AA}^{B_{cis}}$	$\epsilon_{AB}^{B_{cis}}$	$\epsilon_{AA}^{A_{tr}}$	$\epsilon_{AB}^{A_{tr}}$	$\epsilon_{AA}^{B_{tr}}$	$\epsilon_{AB}^{B_{tr}}$
	8	0	0	0	4	0	0	0
$E_{AAAA}^A = 4\varphi_{AA} +$								
	4	2	2	0	2	1	1	0
$E_{AAAB}^A = 3\varphi_{AA} + \varphi_{AB} +$								
	$2 \times 4/6$	$2 \times 4/6$	$2 \times 4/6$	$2 \times 4/6$	0	$2 \times 4/6$	$2 \times 4/6$	0
$\times 4/6$								
	0	$4 \times 2/6$	$4 \times 2/6$	0	$2 \times 2/6$	0	0	$2 \times 2/6$
$\times 2/6$								
$\bar{E}_{AABB}^A = 2\varphi_{AA} + 2\varphi_{AB} +$	$4/3$	$8/3$	$8/3$	$4/3$	$2/3$	$4/3$	$4/3$	$2/3$
	0	2	2	4	0	1	1	2
$E_{ABBB}^A = \varphi_{AA} + 3\varphi_{AB} +$								
	0	0	0	8	0	0	0	4
$E_{BBBB}^A = 4\varphi_{AB} +$								
$J_1^A = E_{AAAB}^A - E_{AAAA}^A = \varphi_{AB} - \varphi_{AA} +$	-4	+2	+2	0	-2	+1	+1	0
$J_2^A = E_{AABB}^A - E_{AAAB}^A = \varphi_{AB} - \varphi_{AA} +$	$-8/3$	$+2/3$	$+2/3$	$+4/3$	$-4/3$	$+1/3$	$+1/3$	$+2/3$
$J_3^A = E_{ABBB}^A - E_{AABB}^A = \varphi_{AB} - \varphi_{AA} +$	$-4/3$	$-2/3$	$-2/3$	$+8/3$	$-2/3$	$-1/3$	$-1/3$	$+4/3$
$J_4^A = E_{BBBB}^A - E_{ABBB}^A = \varphi_{AB} - \varphi_{AA} +$	0	-2	-2	+4	0	-1	-1	+2
$d_{21}^1 = J_2^A - J_1^A =$	$+4/3$	$-4/3$	$-4/3$	$+4/3$	$+2/3$	$-2/3$	$-2/3$	$+2/3$
$d_{32}^1 = J_3^A - J_2^A =$	$+4/3$	$-4/3$	$-4/3$	$+4/3$	$+2/3$	$-2/3$	$-2/3$	$+2/3$
$d_{43}^1 = J_4^A - J_3^A =$	$+4/3$	$-4/3$	$-4/3$	$+4/3$	$+2/3$	$-2/3$	$-2/3$	$+2/3$

**Table A2.** Numbers of the 5-centre effects  $\varepsilon_{ij}^{m(l(k))}$  contributing to the energy of a molecule (A) in a tetrahedral environment

Configuration	$\varepsilon_{AA}^{A(A(A))}$	$\varepsilon_{AB}^{A(A(A))}$	$\varepsilon_{AA}^{A(A(B))}$	$\varepsilon_{AB}^{A(A(B))}$	$\varepsilon_{AA}^{A(B(A))}$	$\varepsilon_{AB}^{A(B(A))}$	$\varepsilon_{AA}^{A(B(B))}$	$\varepsilon_{AB}^{A(B(B))}$
A(AAAA)	108	0	0	0	0	0	0	0
A(AAAB)	24	12	18	0	18	9	0	0
A(AABB)	2	4	8	4	8	16	8	4
A(ABBB)	0	0	0	0	0	9	6	12
A(BBBB)	0	0	0	0	0	0	0	0
	$\varepsilon_{AA}^{B(A(A))}$	$\varepsilon_{AB}^{B(A(A))}$	$\varepsilon_{AA}^{B(A(B))}$	$\varepsilon_{AB}^{B(A(B))}$	$\varepsilon_{AA}^{B(B(A))}$	$\varepsilon_{AB}^{B(B(A))}$	$\varepsilon_{AA}^{B(B(B))}$	$\varepsilon_{AB}^{B(B(B))}$
A(AAAA)	0	0	0	0	0	0	0	0
A(AAAB)	12	6	9	0	0	0	0	0
A(AABB)	4	8	16	8	4	8	4	2
A(ABBB)	0	0	9	18	0	18	12	24
A(BBBB)	0	0	0	0	0	0	0	108

This form has an advantage that the lower-order parameters ( $\delta_i$ ) do not enter higher-order terms; zero value of  $\delta_3$  then means zero contribution from fifth order interactions. In order to get zero contribution of quaternary interactions both  $\delta_3$  and  $\delta_2$  must be zero, which is reasonable because it is difficult to imagine a situation when interactions of the 5-th order exist but quaternary interactions are absent. The physical model of interactions leading to the variation of  $J_i$  according to Eq. (A1) corresponds to the introduction of 5-centre interactions as ternary effects  $\varepsilon_{ij}^{m(l(k))}$ :

$$\psi = \sum_{k \neq j} \sum_j \varepsilon_{ij}^k + \sum_{l \neq k} \sum_{k \neq j} \sum_j \varepsilon_{ij}^{l(k)} + \sum_{m \neq k} \sum_{l \neq k} \sum_{k \neq j} \sum_j \varepsilon_{ij}^{m(l(k))} \quad (\text{A7})$$

Ternary effects can be considered as fractions ( $\gamma$ ) of secondary effects:

$$\varepsilon_{ij}^{m(l(k))} = \gamma^{(m)} \beta^{(l)} \alpha^{(k)} \varphi_{ij} \quad (\text{A8})$$

There are 108 such effects per tetrahedron belonging to 16 types (Table A2). Computations according to this matrix show that non-zero finite differences of third order appear when:

$$\alpha^A \neq \alpha^B, \quad \beta^A \neq \beta^B, \quad \gamma^A \neq \gamma^B \quad (\text{A9})$$

Regularisation bounds used above can be employed in order to diminish the number of variable parameters:

$$\alpha^A = -\alpha^B, \quad \beta^A = -\beta^B, \quad \gamma^A = -\gamma^B \quad (\text{A10})$$

All energies in two quintets (A and B) can thus be defined using 6 parameters:  $\varphi_{AA}$ ,  $\varphi_{BB}$ ,  $\alpha^A$ ,  $\beta^A$ ,  $\gamma^A$ , and  $\kappa$ . Furthermore it can be assumed (as an upper limit of the efficiency of higher order effects) that  $\beta^A = \frac{1}{3}\alpha^A$  and  $\gamma^A = \frac{1}{3}\beta^A$ . Non-ideality parameters arising from *compensated* ternary effects ( $\gamma^B = \gamma^A = \frac{1}{3}\beta^A$  at  $\beta^A = \frac{1}{3}\alpha^A$ ,  $\beta^B = -\beta^A$ ,  $\alpha^B = -\alpha^A$ ) do not considerably differ from similar parameters obtained with  $\gamma^A = \gamma^B = 0$ . The introduction of *non-compensated* ternary effects  $\gamma^A = \frac{1}{3}\beta^A$  at  $\beta^A = \frac{1}{3}\alpha^A$  and  $\alpha^B = -\alpha^A$ ,  $\beta^B = -\beta^A$ ,  $\gamma^B = -\gamma^A$  brings about some changes into non-ideality parameters; they do not, however, change the type of the expected transition.

#### *The Free Energy of a Binary Mixture in a Simple Cubic Lattice*

Similar to the case of the tetrahedral environment, the free energy of a binary mixture of molecules having an octahedral environment can be derived as a function of composition ( $x_A$ ) and degree

of order ( $s$ ):

$$\begin{aligned}
F = & +F_{B_6}^B + (F_{A_6}^A - F_{B_6}^B + D_A + D_B + 6J_1^B - D_B)x_A + [A_2 + B_{20} + (B_{22} - A_2)s^2]x_A^2 \\
& + [A_3 + B_{30} + (B_{32} - A_3)s^2]x_A^3 + [A_4 + B_{40} + B_{42}s^2 + (B_{44} - A_4)s^4]x_A^4 \\
& + [A_5 + B_{50} + (B_{52} + 2A_5)s^2 + (B_{54} - A_5)s^4]x_A^5 + [A_6 + B_{60} + (B_{62} + 5A_6)s^2 \\
& + (B_{64} - 5A_6)s^4 + (B_{66} - A_6)s^6]x_A^6 + (A_7 + B_7)(1 - s^2)(1 + 10s^2 + 5s^4)x_A^7 \\
& + \frac{1}{2}NkT[u_1 \ln u_1 + (1 - u_1) \ln(1 - u_1) + u_2 \ln u_2 + (1 - u_2) \ln(1 - u_2)]
\end{aligned} \tag{A11}$$

in which  $u_1 = (1 + s)x_A$ ,  $u_2 = (1 - s)x_A$  and:

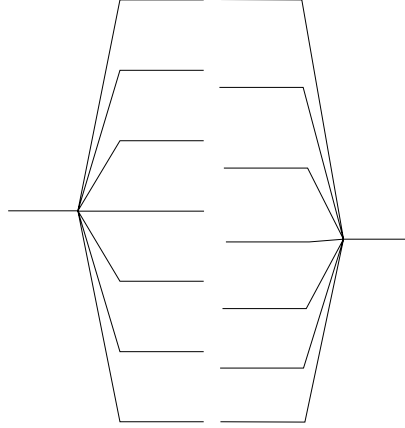
$$\begin{aligned}
A_7 = & -2J_1^A + 4J_2^A - 11J_3^A + 9J_4^A - 6J_5^A + D_A \\
A_6 = & 6J_1^A + 30J_3^A - 30J_4^A + 30J_5^A - 6D_A \\
A_5 = & -15J_1^A - 15J_2^A - 30J_3^A + 30J_4^A - 60J_5^A + 15D_A \\
A_4 = & 20J_1^A + 20J_2^A + 20J_3^A + 60J_5^A - 20D_A \\
A_3 = & -15J_1^A - 15J_2^A - 15J_3^A - 15J_4^A - 30J_5^A + 15D_A \\
A_2 = & 6J_1^A + 6J_2^A + 6J_3^A + 6J_4^A + 6J_5^A - 6D_A \\
B_7 = & -D_B + 2J_1^B - 4J_2^B + 11J_3^B - 9J_4^B + 6J_5^B \\
B_{60} = & D_B - 8J_1^B + 28J_2^B - 47J_3^B + 33J_4^B - 12J_5^B \\
B_{62} = & 15D_B - 60J_1^B + 180J_2^B - 345J_3^B + 255J_4^B - 120J_5^B \\
B_{64} = & 15D_B - 60J_2^B + 15J_3^B + 15J_4^B - 60J_5^B \\
B_{66} = & D_B + 4J_1^B - 20J_2^B + 25J_3^B - 15J_4^B \\
B_{50} = & 21J_1^B - 69J_2^B + 81J_3^B - 39J_4^B + 6J_5^B \\
B_{52} = & 90J_1^B - 330J_2^B + 450J_3^B - 270J_4^B + 60J_5^B \\
B_{54} = & -15J_1^B + 15J_2^B + 45J_3^B - 75J_4^B + 30J_5^B \\
B_{40} = & -35J_1^B + 85J_2^B - 65J_3^B + 15J_4^B \\
B_{42} = & -90J_1^B + 270J_2^B - 270J_3^B + 90J_4^B \\
B_{44} = & 5J_1^B + 5J_2^B - 25J_3^B + 15J_4^B \\
B_{30} = & 35J_1^B - 55J_2^B + 20J_3^B \\
B_{32} = & 45J_1^B - 105J_2^B + 60J_3^B \\
B_{20} = & -21J_1^B + 15J_2^B + D_B - D_B \\
B_{22} = & -9J_1^B + 15J_2^B - D_B + D_B
\end{aligned} \tag{A12}$$

When all asymmetries are zero, *i.e.* when  $J_1^A = J_2^A = J_3^A = J_4^A = J_5^A = J_6^A = J_7^A$  this equation is reduced to that of the model of binary interactions:

$$\begin{aligned}
F = & -(D_A + D_B)(1 - s^2)x_A^2 + (F_{A_6}^A - F_{B_6}^B + D_B + D_A)x_A + F_{B_6}^B \\
& + \frac{1}{2}NkT[u_1 \ln u_1 + (1 - u_1) \ln(1 - u_1) + u_2 \ln u_2 + (1 - u_2) \ln(1 - u_2)]
\end{aligned} \tag{A13}$$

In the case of a regular septet with linearly varying splittings (Fig. A1) employing the relationships between  $J$ -s given by Eq. (A14) it is possible to transform Eq. (A11) into the form equivalent to that of the model of ternary interactions (Eq. (A15)).

$$\begin{aligned}
J_i^A = & J_1^A + (i - 1)\delta_1 \\
D_A = & \sum_1^6 J_i^A = 6J_1^A - \delta_1^A \left( 6 + \sum_1^6 i \right) = 6J_1^A + 15\delta_1
\end{aligned}$$



**Fig. A1.** Transformation of an equidistant septet into the septet with linearly varying splittings

$$\begin{aligned}
 \Delta_i^A &= 6J_i^A - D_A = (6i - 21)\delta_1^A \\
 J_1^A &= \frac{D_A}{6} - \frac{5}{2}\delta_1^A, & \Delta_1^A &= -15\delta_1^A \\
 J_2^A &= \frac{D_A}{6} - \frac{3}{2}\delta_1^A, & \Delta_1^A &= -9\delta_1^A \\
 J_3^A &= \frac{D_A}{6} - \frac{1}{2}\delta_1^A; & \Delta_1^A &= -3\delta_1^A \\
 J_4^A &= \frac{D_A}{6} + \frac{1}{2}\delta_1^A; & \Delta_1^A &= 3\delta_1^A \\
 J_5^A &= \frac{D_A}{6} + \frac{3}{2}\delta_1^A; & \Delta_1^A &= 9\delta_1^A \\
 J_6^A &= \frac{D_A}{6} + \frac{5}{2}\delta_1^A; & \Delta_1^A &= 15\delta_1^A
 \end{aligned} \tag{A14}$$

$$\begin{aligned}
 F &= \left( \begin{array}{c} 15\delta_1^A - 15\delta_1^B \\ -s^2(15\delta_1^A - 15\delta_1^B) \end{array} \right) x_A^3 + \left( \begin{array}{c} -15\delta_1^A + 15\delta_1^B - (-15\delta_1^B + D_A + D_B) \\ s^2(+15\delta_1^A + 15\delta_1^B + (-15\delta_1^B + D_A + D_B)) \end{array} \right) x_A^2 \\
 &+ \left( -15\delta_1^B + D_B + D_A + F_{A_6}^A - F_{B_6}^B \right) x_A + F_{B_6}^B \\
 &+ \frac{1}{2}NkT[u_1 \ln u_1 + (1 - u_1) \ln(1 - u_1) + u_2 \ln u_2 + (1 - u_2) \ln(1 - u_2)]
 \end{aligned} \tag{A15}$$

Similar to the case of a diamond lattice it is possible to transform Eq. (A11) into an equation with contributions from binary, ternary, and quaternary interactions by supposing that splittings in a septet vary according to polynomials of second order. Septets with splittings varying according to the third order polynomial yield the model of 5-centre interactions and so forth.

This shows that irrespective of the number of nearest neighbours taken into account, the behaviour of a system can be described by the model of ternary interactions under the condition that splittings are linearly related. This type of variation corresponds to taking into account primary effects of molecules on binary interactions. In octahedral configurations one has to distinguish cis- and trans-effects (Table A3). However the ratio of contributions of cis- and trans-effects into the splittings of energy levels is constant (see Table A4) allowing one to employ a single effective parameter. Table A4 shows that taking into account primary effects leads to constant finite differences of the first order and hence to a septet with linearly varying splittings.

**Table A3.** Primary effects in octahedral environments

	$\epsilon_{AA}^{A_{cis}}$	$\epsilon_{AB}^{A_{cis}}$	$\epsilon_{AA}^{B_{cis}}$	$\epsilon_{AB}^{B_{cis}}$	$\epsilon_{AA}^{A_{tr}}$	$\epsilon_{AB}^{A_{tr}}$	$\epsilon_{AA}^{B_{tr}}$	$\epsilon_{AB}^{B_{tr}}$
	24	0	0	0	6	0	0	0
	16	4	4	0	4	1	1	0
	10	6	6	2	2	2	2	
	8	8	8	0	4	0	0	2
	6	6	6	6	0	3	3	0
	4	8	8	4	2	1	1	2
	2	6	6	10	0	2	2	2
	0	8	8	8	2	0	0	4
	0	4	4	16	0	1	1	4
	0	0	0	24	0	0	0	6

**Table A4.** Splittings of energy levels computed for octahedral surroundings in terms of binary potentials ( $\varphi_{ij}$ ) and primary effects  $\varepsilon_{ij}^k$ 

	$\varepsilon_{AA}^{A_{cis}}$	$\varepsilon_{AB}^{A_{cis}}$	$\varepsilon_{AA}^{B_{cis}}$	$\varepsilon_{AB}^{B_{cis}}$	$\varepsilon_{AA}^{A_r}$	$\varepsilon_{AB}^{A_r}$	$\varepsilon_{AA}^{B_r}$	$\varepsilon_{AB}^{B_r}$
$E_{AAAAAA}^A = 6\varphi_{AA} +$	24	0	0	0	6	0	0	0
$E_{AAAAAB}^A = 5\varphi_{AA} + \varphi_{AB} +$	16	4	4	0	4	1	1	0
$\bar{E}_{AAAABB}^A = 4\varphi_{AA} + 2\varphi_{AB} +$	48/5	32/5	32/5	8/5	12/5	8/5	8/5	2/5
$\bar{E}_{AAABBB}^A = 3\varphi_{AA} + 3\varphi_{AB} +$	24/5	36/5	36/5	24/5	6/5	9/5	9/5	6/5
$\bar{E}_{AABBBB}^A = 2\varphi_{AA} + 4\varphi_{AB} +$	8/5	32/5	32/5	48/5	2/5	8/5	8/5	12/5
$E_{ABBBBB}^A = \varphi_{AA} + 5\varphi_{AB} +$	0	4	4	16	0	1	1	4
$E_{BBBBBB}^A = 6\varphi_{AA} +$	0	0	0	24	0	0	0	6
$J_1^A = E_{AAAAAB}^A - E_{AAAAAA}^A = \varphi_{AB} - \varphi_{AA} +$	-8	+4	+4	0	-2	+1	+1	0
$J_2^A = E_{AAAABB}^A - E_{AAAAAB}^A = \varphi_{AB} - \varphi_{AA} +$	-32/5	+12/5	+12/5	+8/5	-8/5	+3/5	+3/5	+2/5
$J_3^A = E_{AAABBB}^A - E_{AAAABB}^A = \varphi_{AB} - \varphi_{AA} +$	-24/5	+4/5	+4/5	+16/5	-6/5	+1/5	+1/5	+4/5
$J_4^A = E_{AABBBB}^A - E_{AAABBB}^A = \varphi_{AB} - \varphi_{AA} +$	-16/5	-4/5	-4/5	+24/5	-4/5	-1/5	-1/5	+6/5
$J_5^A = E_{ABBBBB}^A - E_{AABBBB}^A = \varphi_{AB} - \varphi_{AA} +$	-8/5	-12/5	-12/5	+32/5	-2/5	-3/5	-3/5	+8/5
$J_6^A = E_{BBBBBB}^A - E_{ABBBBB}^A = \varphi_{AB} - \varphi_{AA} +$	0	-4	-4	+8	0	-1	-1	+2
$d_{21}^1 = J_2^A - J_1^A =$	+8/5	-8/5	-8/5	+8/5	+2/5	-2/5	-2/5	+2/5
$d_{32}^1 = J_3^A - J_2^A =$	+8/5	-8/5	-8/5	+8/5	+2/5	-2/5	-2/5	+2/5
$d_{43}^1 = J_4^A - J_3^A =$	+8/5	-8/5	-8/5	+8/5	+2/5	-2/5	-2/5	+2/5
$d_{54}^1 = J_5^A - J_4^A =$	+8/5	-8/5	-8/5	+8/5	+2/5	-2/5	-2/5	+2/5
$d_{65}^1 = J_6^A - J_5^A =$	+8/5	-8/5	-8/5	+8/5	+2/5	-2/5	-2/5	+2/5

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