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The Role of Binary and Many-center Molecular Interactions in Spin Crossover in the Solid State. Part III. Expressing Many-body Interactions

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Summary. The approach of molecular potentials describing the shape of transition curves of spin crossover in the solid state developed earlier has been extended to many-body interactions characterized by the *Axilrod-Teller* potential. An improved procedure for the minimization of energy developed for this case is presented. Calculations for systems involving *Lennard-Jones*, electric dipole–dipole, and dispersive *Axilrod-Teller* triple interactions yield non-zero asymmetries of splittings in expanded/compressed systems alone. The excess energy is unaffected by the *Axilrod-Teller* potential. Triple interactions of the *Axilrod-Teller* type thus increase the sensitivity of a transition curve towards compression.

Another approach presented employs the deviations of molecules from positions of mechanical equilibrium set up by the known binary potential. In the approximation of small perturbations these deviations are proportional to the gradients of many-center potentials. This allows one to parametrically define non-ideality parameters as functions of gradients of triple potentials of unknown types. Employing regularization bounds an adequate parameterization of experimental transition curve of spin crossover has been achieved in terms of parameters of *Lennard-Jones* potential and relative deviations of molecules from the position of mechanical equilibrium.

Keywords. Solid state; Thermodynamics; Spin crossover; Molecular interactions; Many-body interactions.

Introduction

Many-body interactions significantly contribute towards the free energy of condensed systems [1–4]. In our previous publications [5–9] we have developed a theoretical model of a simple chemical equilibrium in the solid state:

$$A \rightleftharpoons B \qquad (1)$$

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This formalism takes into account both binary and triple interactions characterized by formal non-ideality parameters, *viz.* the excess energy (ΔE_{ex}) and asymmetries of splittings (Δ^{A}, Δ^{B}) of energy levels of participating molecules. These parameters have been derived from energies of molecules A and B in all possible surroundings along one coordinate, *i.e.* in configurations AAA, AAB, BAB, BBB, ABB, and ABA. In this formalism the excess energy is a microscopic parameter equal the sum of the main splittings of energy levels: $\Delta E_{ex} = E_{\mathrm{BAB}} - E_{\mathrm{AAA}} + E_{\mathrm{ABA}} - E_{\mathrm{BBB}}$. The asymmetries reflect the difference in effects of the first and second substitutions in molecular surroundings: $\Delta^{\mathrm{A}} = F_{\mathrm{AAB}} - F_{\mathrm{AAA}} + F_{\mathrm{AAB}} - F_{\mathrm{BAB}}$, $\Delta^{\mathrm{B}} = F_{\mathrm{BBA}} - F_{\mathrm{BBB}} + F_{\mathrm{BBA}} - F_{\mathrm{ABA}}$. When binary interactions are only taken into account the asymmetries are zero whereas the excess energy equals the formal excess energy of the theory of regular solutions.

The developed formalism provided for adequate parameterization of all known types of the spin crossover equilibrium between low-spin (A, LS) and high-spin (B, HS) isomers, *viz.* gradual, abrupt and two-step spin crossover (Fig. 1). Gradual transitions correspond to linear *van't Hoff* plots and can be described in a pseudo-ideal approximation. Abrupt spin crossover originates from strong homo-molecular interactions characterized by large positive excess energies and leading to the separation of HS-rich and LS-rich phases. The two-step spin crossover originates from strong hetero-molecular (HS–LS) interactions leading to the formation of ordered structures. It has been shown [5, 8] that many-body interactions play a considerable role in spin crossover: the two-step spin crossover may be caused by large negative excess energies as well as by large positive asymmetries of splittings or combination of these parameters.

In Ref. [9] we have expressed non-ideality parameters in terms of *binary* molecular potentials. Binary interactions mainly contribute towards the excess energy whereas the asymmetries of splittings arise from either *selective* binary interactions or many-body interactions.

Triple interactions considered as perturbations of binary interactions can be taken into account as yielding a separate contribution towards the total energy:

$$E = \sum_{ij} \varphi_{ij} + \sum_{ijk} \psi_{ijk} \tag{2}$$

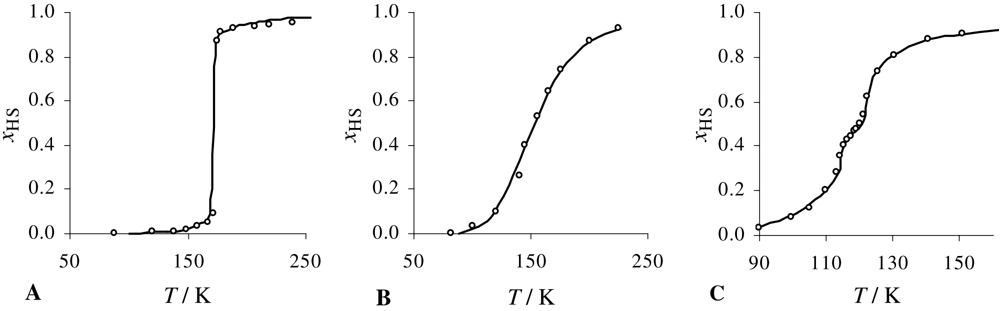

Fig. 1. Three basic types of spin crossover: abrupt transition in [Fe(*phen*)$_2$(NCS)$_2$] (**A**, data from Ref. [10]), gradual transition in [Fe(2-*pic*)$_3$]Cl$_2$CH$_3$OH (**B**, data from Ref. [11]), and two-step spin crossover in [Fe(2-*pic*)$_3$]Cl$_2$CH$_3$CH$_2$OH (**C**, data from Ref. [12]); x_{HS} is the mol fraction of HS species

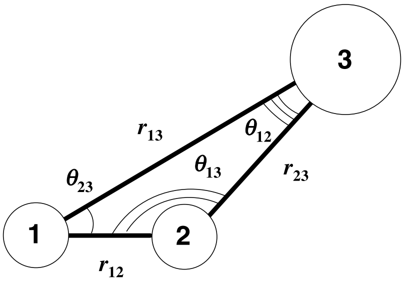

Fig. 2. Geometric parameters employed in the calculation of the *Axilrod-Teller* potential

In a system of molecules interacting *via* dispersive forces a third molecule changes the instantaneous electric moments of two other molecules. Corresponding potential is known under the name of the *Axilrod-Teller* triplet potential [13]:

$$\psi_{123} = \frac{3}{4} h\nu \frac{\alpha_1\alpha_2\alpha_3}{r_{12}^3 r_{13}^3 r_{23}^3} (3\cos\theta_{12}\cos\theta_{13}\cos\theta_{23} + 1) \tag{3}$$

in which α_i are polarizabilities, r_{ij} are intermolecular distances, θ_{ij} are angles opposite to r_{ij} (Fig. 2), and ν is the mean electronic frequency:

$$\nu = \frac{3\nu_1\nu_2\nu_3}{\nu_1\nu_2 + \nu_1\nu_3 + \nu_2\nu_3} \tag{4}$$

Parameters of the *Axilrod-Teller* potential can be expressed *via* parameters of the *Lennard-Jones* potential. The constant B in the attractive part of the *Lennard-Jones* potential ($\varphi_{ij} = -B_{ij}/{r_{ij}}^6$) is proportional to the square of polarisability [14]:

$$B = 0.68\, h\nu\alpha^2\sqrt{m} \tag{4a}$$

in which m is the number of electrons involved in the dispersion process. The product of polarizabilities in Eq. (3) can be combined with $(3/4)h\nu$, which yields $1.103\alpha_i B_{jk}/\sqrt{m}$:

$$\psi_{123} = \frac{1.103}{\sqrt{m}} \frac{\alpha_1}{r_{13}^3} \frac{B_{23}}{r_{12}^3 r_{23}^3} f(\theta) \tag{5}$$

Three-center potential thus equals approximately $\alpha_1 r_{13}^{-3} m^{-1/2} f(\theta)$ multiplied by the attractive part of the *Lennard-Jones* potential. The constant B_{ij} of the *Lennard-Jones* potential can be expressed in terms of coordinates of the point of mechanical equilibrium (ε_{ij} and $a_{ij} = \sigma_{ij} \times 2^{1/6}$):

$$B_{ij} = 4\varepsilon_{ij}\sigma_{ij}^6 \tag{6}$$

Therefore:

$$\psi_{123} \approx \varepsilon_{23} \frac{4f(\theta)}{\sqrt{m}} \frac{\alpha_1\sigma_{23}^6}{r_{13}^3 r_{12}^3 r_{23}^3} \tag{6a}$$

The polarizability α_i approximately equals the molecular volume [15]:

$$\alpha \approx 0.7v = \frac{0.7\pi a_{ij}^3}{6} = \frac{0.7\sqrt{2}\pi\sigma_{ij}^3}{6} = 0.51\sigma^3 \tag{7}$$

Hence:

$$\psi_{123} \approx \varepsilon_{23} \frac{2f(\theta)}{\sqrt{m}} \frac{\sigma_{11}^3 \sigma_{23}^6}{r_{13}^3 r_{12}^3 r_{23}^3} \tag{8}$$

For linear chains of three molecules employed in the model [5–9] (AAA, AAB, *etc.*) the geometric factor $f(\theta) = -2$, hence:

$$\psi_{123} \approx -\frac{4(\varepsilon_{12}\varepsilon_{23}\varepsilon_{13})^{\frac{1}{3}}}{\sqrt{m}} \left(\frac{\sigma_{12}\sigma_{23}\sigma_{13}}{r_{13}r_{12}r_{23}}\right)^3 \tag{9}$$

Writing this expression *via* the *van der Waals* diameters one obtains:

$$\psi_{123} \approx -\frac{2(\varepsilon_{12}\varepsilon_{23}\varepsilon_{13})^{\frac{1}{3}}}{\sqrt{2m}} \left(\frac{a_{12}a_{23}a_{13}}{r_{13}r_{12}r_{23}}\right)^3 \tag{10}$$

The effective number of electrons taking part in dispersive interactions (m) for spin crossover molecules apparently lies between 1 and 10. A general form of such a three-center potential thus is:

$$\psi_{123} \approx -\kappa_{123}(\varepsilon_{12}\varepsilon_{23}\varepsilon_{13})^{\frac{1}{3}} \left(\frac{a_{12}a_{23}a_{13}}{r_{13}r_{12}r_{23}}\right)^3 \tag{11}$$

in which $\kappa_{123} = 0.44$ for $m = 10$ and $\kappa_{123} = 1.39$ for $m = 1$.

In the present paper we shall explore possible effects of many-body interactions on equilibria in the solid state employing two methods: (i) introducing the *Axilrod-Teller* potential and (ii) characterizing many-body interactions by their effects on intermolecular distances.

Results and Discussions

A Model System Involving Lennard-Jones, Axilrod-Teller and Electric Dipole–Dipole Interactions

Minimization of energy. The excess energy and asymmetries of splittings have been obtained as [9]:

$$\Delta^{\mathrm{A}} = 3(2\psi_{\mathrm{AAB}} - \psi_{\mathrm{BAB}} - \psi_{\mathrm{AAA}}) \tag{12}$$

$$\Delta^{\mathrm{B}} = 3(2\psi_{\mathrm{ABB}} - \psi_{\mathrm{ABA}} - \psi_{\mathrm{BBB}}) \tag{12a}$$

$$\Delta E_{ex} = 3(4\varphi_{\mathrm{AB}} - 2\varphi_{\mathrm{AA}} - 2\varphi_{\mathrm{BB}} + \psi_{\mathrm{ABA}} - \psi_{\mathrm{BBB}} + \psi_{\mathrm{BAB}} - \psi_{\mathrm{AAA}}) \tag{12b}$$

In order to compute these parameters the *van der Waals* diameters and molecular distances must be optimized for the minimum of energy. This does not present any serious problem for systems with purely binary interactions (see Ref. [9]), however taking into account triple interactions makes this procedure more complicated.

Consider a system involving *Lennard-Jones*, *Axilrod-Teller*, and electric dipole–dipole interactions. The potential energy of such a system can be written as:

$$\varphi_{123} = \varphi_{bin} + \psi_{123} \tag{13}$$

in which ψ_{123} is given by Eq. (11) and $\varphi_{bin} = {\varphi_{12}}^0 + {\varphi_{23}}^0$ can be written as:

$$\begin{aligned}\varphi_{bin} = \varepsilon_{12}&\left[\left(\frac{a_{12}}{r_{12}}\right)^{12} - 2\left(\frac{a_{12}}{r_{12}}\right)^{6} - \frac{\mu_1\mu_2}{\varepsilon_{12}a_{12}^3}\left(\frac{a_{12}}{r_{12}}\right)^{3}\right] \\ + \varepsilon_{23}&\left[\left(\frac{a_{23}}{r_{23}}\right)^{12} - 2\left(\frac{a_{23}}{r_{23}}\right)^{6} - \frac{\mu_2\mu_3}{\varepsilon_{23}a_{23}^3}\left(\frac{a_{23}}{r_{23}}\right)^{3}\right]\end{aligned} \tag{14}$$

Conditions of the mechanical equilibrium can be written as:

$$\begin{aligned}\mathrm{d}\varphi_{123} &= \left(\frac{\partial\varphi}{\partial r_{12}}\right)_{r_{23}}\mathrm{d}r_{12} + \left(\frac{\partial\varphi}{\partial r_{23}}\right)_{r_{\mathrm{AA}}}\mathrm{d}r_{23} \\ &= \left(\frac{\mathrm{d}\varphi_{12}}{\mathrm{d}r_{12}} + \frac{\partial\psi_{123}}{\partial r_{12}}\right)\mathrm{d}r_{12} + \left(\frac{\mathrm{d}\varphi_{23}}{\mathrm{d}r_{23}} + \frac{\partial\psi_{123}}{\partial r_{23}}\right)\mathrm{d}r_{23} = 0\end{aligned} \tag{14a}$$

For symmetric configurations: AAA, BBB, BAB, and ABA all potentials are functions of one variable ($r_{12} = r_{23}$) and conditions of Eq. (14a) can be written in a relatively simple form:

$$\begin{aligned}\frac{\mathrm{d}\varphi_{\mathrm{AAA}}}{\mathrm{d}r_{\mathrm{AA}}} &= 2\frac{\mathrm{d}\varphi_{\mathrm{AA}}}{\mathrm{d}r_{\mathrm{AA}}} + \frac{\mathrm{d}\psi_{\mathrm{AAA}}}{\mathrm{d}r_{\mathrm{AA}}} \\ &= -\frac{24\varepsilon_{\mathrm{AA}}}{r_{\mathrm{AA}}}\left(\frac{a_{\mathrm{AA}}}{r_{\mathrm{AA}}}\right)^3\left[\left(\frac{a_{\mathrm{AA}}}{r_{\mathrm{AA}}}\right)^9 - \left(\frac{a_{\mathrm{AA}}}{r_{\mathrm{AA}}}\right)^3 - \frac{\mu_{\mathrm{AA}}^2}{4\varepsilon_{\mathrm{AA}}a_{\mathrm{AA}}^3} - \frac{3\kappa}{64}\frac{\varepsilon_{\mathrm{AAA}}}{\varepsilon_{\mathrm{AA}}}\left(\frac{a_{\mathrm{AA}}}{r_{\mathrm{AA}}}\right)^6\right] = 0\end{aligned} \tag{15}$$

$$\begin{aligned}\frac{\mathrm{d}\varphi_{\mathrm{BBB}}}{\mathrm{d}r_{\mathrm{BB}}} &= 2\frac{\mathrm{d}\varphi_{\mathrm{BB}}}{\mathrm{d}r_{\mathrm{BB}}} + \frac{\mathrm{d}\psi_{\mathrm{BBB}}}{\mathrm{d}r_{\mathrm{BB}}} \\ &= -\frac{24\varepsilon_{\mathrm{BB}}}{r_{\mathrm{BB}}}\left(\frac{a_{\mathrm{BB}}}{r_{\mathrm{BB}}}\right)^3\left[\left(\frac{a_{\mathrm{BB}}}{r_{\mathrm{BB}}}\right)^9 - \left(\frac{a_{\mathrm{BB}}}{r_{\mathrm{BB}}}\right)^3 - \frac{\mu_{\mathrm{BB}}^2}{4\varepsilon_{\mathrm{BB}}a_{\mathrm{BB}}^3} - \frac{3\kappa}{64}\frac{\varepsilon_{\mathrm{BBB}}}{\varepsilon_{\mathrm{BB}}}\left(\frac{a_{\mathrm{BB}}}{r_{\mathrm{BB}}}\right)^6\right] = 0\end{aligned} \tag{16}$$

$$\begin{aligned}\frac{\mathrm{d}\varphi_{\mathrm{BAB}}}{\mathrm{d}r_{\mathrm{AB}}} &= 2\frac{\mathrm{d}\varphi_{\mathrm{AB}}}{\mathrm{d}r_{\mathrm{AB}}} + \frac{\mathrm{d}\psi_{\mathrm{BAB}}}{\mathrm{d}r_{\mathrm{AB}}} \\ &= -\frac{24\varepsilon_{\mathrm{AB}}}{r_{\mathrm{AB}}}\left(\frac{a_{\mathrm{AB}}}{r_{\mathrm{AB}}}\right)^3\left[\left(\frac{a_{\mathrm{AB}}}{r_{\mathrm{AB}}}\right)^9 - \left(\frac{a_{\mathrm{AB}}}{r_{\mathrm{AB}}}\right)^3 - \frac{\mu_A\mu_B}{4\varepsilon_{\mathrm{AB}}a_{\mathrm{AB}}^3} - \frac{3\kappa}{64}\frac{\varepsilon_{\mathrm{BAB}}}{\varepsilon_{\mathrm{AB}}}\alpha_{\mathrm{B}}^3\left(\frac{a_{\mathrm{AB}}}{r_{\mathrm{AB}}}\right)^6\right] = 0\end{aligned} \tag{17}$$

$$\begin{aligned}\frac{\mathrm{d}\varphi_{\mathrm{ABA}}}{\mathrm{d}r_{\mathrm{AB}}} &= 2\frac{\mathrm{d}\varphi_{\mathrm{AB}}}{\mathrm{d}r_{\mathrm{AB}}} + \frac{\mathrm{d}\psi_{\mathrm{ABA}}}{\mathrm{d}r_{\mathrm{AB}}} \\ &= -\frac{24\varepsilon_{\mathrm{AB}}}{r_{\mathrm{AB}}}\left(\frac{a_{\mathrm{AB}}}{r_{\mathrm{AB}}}\right)^3\left[\left(\frac{a_{\mathrm{AB}}}{r_{\mathrm{AB}}}\right)^9 - \left(\frac{a_{\mathrm{AB}}}{r_{\mathrm{AB}}}\right)^3 - \frac{\mu_{\mathrm{A}}\mu_{\mathrm{B}}}{4\varepsilon_{\mathrm{AB}}a_{\mathrm{AB}}^3} - \frac{3\kappa}{64}\frac{\varepsilon_{\mathrm{ABA}}}{\varepsilon_{\mathrm{AB}}}\alpha_{\mathrm{A}}^{-3}\left(\frac{a_{\mathrm{AB}}}{r_{\mathrm{AB}}}\right)^6\right] = 0\end{aligned} \tag{18}$$

in which $\alpha_\mathrm{A} = a_\mathrm{AB}/a_\mathrm{AA}$; $\alpha_\mathrm{B} = a_\mathrm{BB}/a_\mathrm{AB}$. These equations are cubic equations of the type:

$$y^3 - py^2 - y - r = 0 \tag{19}$$

easily solvable by numeric methods. Note that, equilibrium values of r_AB in BAB and ABA are different due to different three-center potentials ψ_ABA and ψ_BAB.

For the asymmetric configuration AAB the condition of mechanical equilibrium can be written in two forms convenient for calculations of either r_AA or r_AB:

$$\frac{\mathrm{d}\varphi}{\mathrm{d}r_\mathrm{AA}} = \frac{\mathrm{d}\varphi_\mathrm{AA}}{\mathrm{d}r_\mathrm{AA}} + \frac{\partial\psi_\mathrm{AAB}}{\partial r_\mathrm{AA}} + \left(\frac{\mathrm{d}\varphi_\mathrm{AB}}{\mathrm{d}r_\mathrm{AB}} + \frac{\partial\psi_\mathrm{AAB}}{\partial r_\mathrm{AB}}\right)\frac{\mathrm{d}r_\mathrm{AB}}{\mathrm{d}r_\mathrm{AA}} = 0 \tag{20}$$

$$\frac{\mathrm{d}\varphi}{\mathrm{d}r_\mathrm{AB}} = \frac{\mathrm{d}\varphi_\mathrm{AB}}{\mathrm{d}r_\mathrm{AB}} + \frac{\partial\psi_\mathrm{AAB}}{\partial r_\mathrm{AB}} + \left(\frac{\mathrm{d}\varphi_\mathrm{AA}}{\mathrm{d}r_\mathrm{AA}} + \frac{\partial\psi_\mathrm{AAB}}{\partial r_\mathrm{AA}}\right)\frac{\mathrm{d}r_\mathrm{AA}}{\mathrm{d}r_\mathrm{AB}} = 0 \tag{21}$$

Assuming r_AA and r_AB to be independent variables ($\mathrm{d}r_\mathrm{AA}/\mathrm{d}r_\mathrm{AB} = 0$, $\mathrm{d}r_\mathrm{AB}/\mathrm{d}r_\mathrm{AA} = 0$), one obtains the conditions $\frac{\mathrm{d}\varphi_\mathrm{AAB}}{\mathrm{d}r_\mathrm{AA}} = 0$, $\frac{\mathrm{d}\varphi_\mathrm{AAB}}{\mathrm{d}r_\mathrm{AB}} = 0$ as:

$$\left(\frac{a_\mathrm{AA}}{r_\mathrm{AA}}\right)^9 - \left(\frac{a_\mathrm{AA}}{r_\mathrm{AA}}\right)^3 - \frac{\mu_\mathrm{A}^2}{4\varepsilon_\mathrm{AA}a_\mathrm{AA}^3} - \frac{\kappa\varepsilon_\mathrm{AAB}}{32\varepsilon_\mathrm{AA}}\left(\frac{a_\mathrm{AA}}{r_\mathrm{AA}}\right)^6\left(\frac{\alpha_\mathrm{A}}{\rho_\mathrm{A}}\right)^6\left(\frac{2\rho_\mathrm{A}}{1+\rho_\mathrm{A}}\right)^3\frac{2+\rho_\mathrm{A}}{1+\rho_\mathrm{A}} = 0 \tag{22}$$

$$\left(\frac{a_\mathrm{AB}}{r_\mathrm{AB}}\right)^9 - \left(\frac{a_\mathrm{AB}}{r_\mathrm{AB}}\right)^3 - \frac{\mu_\mathrm{A}\mu_B}{4\varepsilon_\mathrm{AB}a_\mathrm{AB}^3} - \frac{\kappa\varepsilon_\mathrm{AAB}}{32\varepsilon_\mathrm{AB}}\left(\frac{a_\mathrm{AB}}{r_\mathrm{AB}}\right)^6\left(\frac{\rho_\mathrm{A}}{\alpha_\mathrm{A}}\right)^3\left(\frac{2\rho_\mathrm{A}}{1+\rho_\mathrm{A}}\right)^3\frac{2\rho_\mathrm{A}+1}{1+\rho_\mathrm{A}} = 0 \tag{23}$$

in which $\rho_\mathrm{A} = r_\mathrm{AB}/r_\mathrm{AA}$. In general, r_AA and r_AB must be found as a joint solution of this system of two equations that requires a complicated iterative procedure. Fortunately the ratio $\rho_\mathrm{A} = r_\mathrm{AB}/r_\mathrm{AA}$ can be considered as a quasi-constant equal to the ratio of corresponding distances in the prototype compound (see Ref. [9]). In such a case Eqs. (22) and (23) can be solved separately with respect to r_AA and r_AB. A similar set of equations can be derived for the configuration BBA:

$$\left(\frac{a_\mathrm{BB}}{r_\mathrm{BB}}\right)^9 - \left(\frac{a_\mathrm{BB}}{r_\mathrm{BB}}\right)^3 - \frac{\mu_B^2}{4\varepsilon_\mathrm{BB}a_\mathrm{BB}^3} - \frac{\kappa\varepsilon_\mathrm{BBA}}{32\varepsilon_\mathrm{BB}}\left(\frac{a_\mathrm{BB}}{r_\mathrm{BB}}\right)^9\left(\frac{\rho_\mathrm{B}}{\alpha_\mathrm{B}}\right)^6\left(\frac{2}{1+\rho_\mathrm{B}}\right)^3\frac{2\rho_\mathrm{B}+1}{1+\rho_\mathrm{B}} = 0 \tag{24}$$

$$\left(\frac{a_\mathrm{AB}}{r_\mathrm{AB}}\right)^9 - \left(\frac{a_\mathrm{AB}}{r_\mathrm{AB}}\right)^3 - \frac{\mu_A\mu_\mathrm{B}}{4\varepsilon_\mathrm{AB}a_\mathrm{AB}^3} - \frac{\kappa\varepsilon_\mathrm{BBA}}{32\varepsilon_\mathrm{AB}}\left(\frac{a_\mathrm{AB}}{r_\mathrm{AB}}\right)^9\left(\frac{\alpha_\mathrm{B}}{\rho_\mathrm{B}}\right)^3\left(\frac{2}{1+\rho_\mathrm{B}}\right)^3\frac{2+\rho_\mathrm{B}}{1+\rho_\mathrm{B}} = 0 \tag{25}$$

in which $\rho_\mathrm{B} = r_\mathrm{BB}/r_\mathrm{AB}$ is considered as a quasi-constant.

The optimization procedure starts with the minimization of energy in AAA and BBB configurations by adjusting *van der Waals* diameters a_AA and a_BB according to Eqs. (15) and (16) at constant $r_\mathrm{AA} = 10.739$ Å, $r_\mathrm{BB} = 10.948$ Å, $\mu_\mathrm{B} = 22.426$ D, and $\mu_\mathrm{A} = 22.812$ D (data for the prototype compound, see Ref. [9]). The parameter a_AB is calculated according to the additivity rule. The depths of *Lennard-Jones*

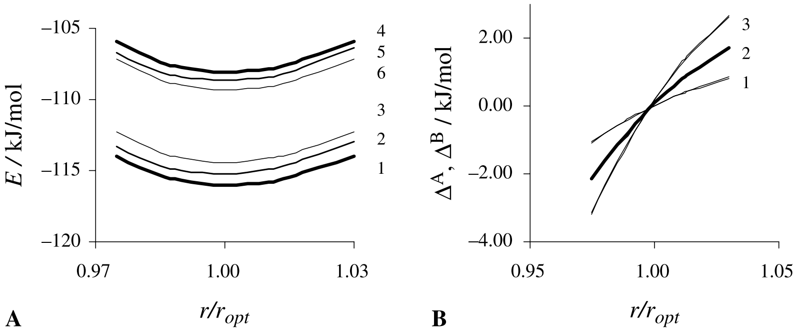

Fig. 3. Effect of the *Axilrod-Teller* potential on the energy levels computed for model system involving *Axilrod-Teller*, *Lennard-Jones*, and electric dipole–dipole potentials (**A**, $\kappa_{123} = 0.4$; curves: 1, 2, 3, 4, 5, and 6 correspond to AAA, AAB, BAB, BBB, BBA, and ABA); the right-hand graph (**B**) shows dependencies of the asymmetries $\Delta^{A(B)}$ on compression/expansion computed for $\kappa_{123} = 0.4$ (1), 0.8 (2) and 1.2 (3)

potentials have been fixed at $\varepsilon_{AA} = 12\,\mathrm{kJ/mol}$ and $\varepsilon_{BB} = 14\,\mathrm{kJ/mol}$. The depth of hetero-molecular potential has been calculated according to *Berthelot*'s rule. Employing these parameters the distances r_{AA}, r_{AB}, and r_{BB} in configurations AAB, BAB, BBA, and ABA are optimized for the minima of energy.

Non-ideality parameters. The combination of the *Axilrod-Teller* ($\kappa_{123} = 0.4$), *Lennard-Jones*, and electric dipole–dipole potentials yields potential curves shown in Fig. 3A. The asymmetry of splitting becomes visible at very large compressions/expansions (*ca*. 3%). According to the data in Table 1 the *Axilrod-Teller* potential does not practically change the excess energy (ΔE_{ex}) at any compression. The asymmetries of splittings at zero compression ($r/r_{opt} = 1$) are negligibly small, (see also Fig. 3B). In compressed/expanded systems the *Axilrod-Teller* potential brings about considerable asymmetries $\Delta^{A(B)}$ (Fig. 3B), that are positive in expanded systems and negative in compressed ones.

Table 1. Non-ideality parameters computed for model system involving *Axilrod-Teller*, *Lennard-Jones*, and electric ($\mu_A = 22.812$ D, $\mu_B = 22.426$ D) dipole–dipole potentials

κ_{123}	r/r_{opt}	D_A / kJ/mol	D_B / kJ/mol	ΔE_{ex} / kJ/mol	Δ^A / kJ/mol	Δ^B / kJ/mol
	0.990	5.142	−4.058	1.084	0.000	0.000
0.000	1.000	5.122	−4.042	1.080	0.000	0.000
	1.010	5.138	−4.055	1.083	0.000	0.000
	0.990	4.863	−3.775	1.088	−0.357	−0.366
0.400	1.000	4.845	−3.757	1.087	0.022	0.023
	1.010	4.860	−3.772	1.088	0.340	0.348
	0.990	4.574	−3.482	1.093	−0.682	−0.698
0.800	1.000	4.557	−3.463	1.094	0.081	0.084
	1.010	4.571	−3.478	1.092	0.720	0.737
	0.990	4.274	−3.178	1.097	−0.974	−0.995
1.200	1.000	4.258	−3.157	1.101	0.179	0.184
	1.010	4.271	−3.174	1.097	1.143	1.169

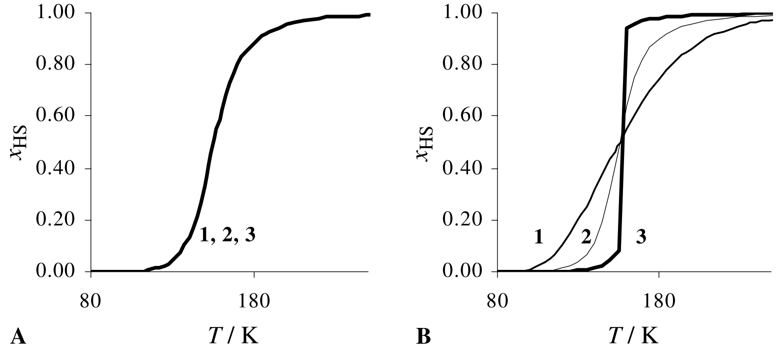

Fig. 4. Increased sensitivity of the shape of spin crossover transition curve towards compression as a result of triple interactions: transition curves in the absence of triple interactions ($\kappa_{123} = 0$, **A**) computed for $r/r_{opt} = 0.98$ (1), 1.00 (2), and 1.03 (3) overlay whereas the same curves computed for $\kappa_{123} = 1.2$ (**B**) show different types of transitions

At linear compression of the order ±1% (volume compression ±3%, required pressure *ca.* 30 kbar) one can expect asymmetries of the order $\Delta^{A(B)} \approx \pm 1$ kJ/mol at $\kappa_{123} = 1.2$. These effects can be interpreted as an increased sensitivity of the shape of transition curve towards compression.

In the absence of triple interactions ($\kappa_{123} = 0$) a compression (expansion) within $r/r_{opt} = 0.98$–1.3 does not change the shape of transition curve (Fig. 4A, energy and entropy of spin crossover are supposed not to be changed by compression/expansion).

In the presence of triple interactions ($\kappa_{123} = 1.2$) the variation of r/r_{opt} in the same range brings about a conversion of the gradual spin crossover (curve 1, Fig. 4B) into an abrupt one (curve 3, Fig. 4B). The increased sensitivity of the shape of transition curves towards compression seems to be the only effect of triple interactions of the *Axilrod-Teller* type. Negative asymmetries arising from compression only decrease the slope of transition curves and do not bring about any critical phenomena. The two-step spin crossover can be expected as a combination of positive asymmetries (in expanded systems) with a negative background excess energy. The overall effect of the *Axilrod-Teller* interactions is not significant, as might be expected for systems with purely dispersive interactions.

Many-body Potentials Represented via their Gradients

The strength of the actual many-body interaction can be higher than that of the purely dispersive forces. For example, many-center exchange interactions in alkali halide crystals contribute up to several percents of the total lattice energy [1], *i.e.* up to 10 kJ/mol. The actual radial dependence of the energy of triple interactions may be complicated and in general unknown. However the energy of many-body interactions can be calculated as an increase in the energy due to the deflection of a molecule from the position corresponding to the minimum of the binary potential. An unknown many-center potential is thus defined in terms of parameters of the binary potential in which the deviation plays the role of the conversion coefficient. It is not difficult to show that in the case of small perturbations the deflection from the point of mechanical equilibrium is proportional to the gradient of the unknown potential.

Let us consider a system involving a known binary potential φ_{ij} and an unknown many-body potential ψ:

$$u = \varphi_{ij} + \psi \tag{26}$$

Suppose that the roots (r^0_{ij}) of equations defining the minima of binary potentials are known for all pairs:

$$\left(\frac{\mathrm{d}\varphi_{ij}}{\mathrm{d}r_{ij}}\right)_{r^0_{ij}} = 0 \tag{27}$$

If ψ is a small perturbation then the actual distance in a given pair can be written as:

$$r_{ij} = r^0_{ji} + \delta_{ij} \tag{28}$$

in which δ is a small deflection. In this case the derivative of the total potential $\mathrm{d}u/\mathrm{d}r_{ij}$ can be partly linearised in the vicinity of the point r^0_{ji} as:

$$\frac{\mathrm{d}u}{\mathrm{d}r_{ij}} = \left(\frac{\mathrm{d}\varphi_{ij}}{\mathrm{d}r_{ij}}\right)_{r^0_{ij}} + \left(\frac{\mathrm{d}^2\varphi_{ij}}{\mathrm{d}r^2_{ij}}\right)_{r^0_{ij}} \left(r_{ij} - r^0_{ij}\right) + \frac{\mathrm{d}\psi}{\mathrm{d}r_{ij}} \tag{29}$$

The condition of mechanical equilibrium involving the total potential:

$$\left(\frac{\mathrm{d}u}{\mathrm{d}r_{ij}}\right)_{r^0_{ij}+\delta} = \left(\frac{\mathrm{d}^2\varphi_{ij}}{\mathrm{d}r^2_{ij}}\right)_{r^0_{ij}} \delta + \left(\frac{\mathrm{d}\psi}{\mathrm{d}r_{ij}}\right)_{r^0_{ij}+\delta} = 0 \tag{30}$$

yields the deflection δ proportional to the gradient of ψ:

$$\delta_{ij} = -\left(\frac{\mathrm{d}\psi}{\mathrm{d}r_{ij}}\right)_{r^0_{ij}+\delta} \Big/ \left(\frac{\mathrm{d}^2\varphi_{ij}}{\mathrm{d}r^2_{ij}}\right)_{r^0_{ij}} \tag{31}$$

The proportionality coefficient equals the inverse second derivative of the binary potential in the point of its minimum. The same relationship can be written as:

$$\left(\frac{\mathrm{d}\psi}{\mathrm{d}r_{ij}}\right)_{r^0_{ij}+\delta} = -\delta_{ij} \left(\frac{\mathrm{d}^2\varphi_{ij}}{\mathrm{d}r^2_{ij}}\right)_{r^0_{ij}} \tag{32}$$

which means that the gradient of the many-body potential is proportional to the deflection of the molecule from the point of the minimum of the binary potential.

Deflections from the point of mechanical equilibrium can be conveniently characterized in terms of relative deviations α_{ij}: $r_{ij} = r^0_{ji}(1 + \alpha_{ij})$. Equation (32) is then transformed into:

$$\left(\frac{\mathrm{d}\psi}{\mathrm{d}r_{ij}}\right)_{r^0_{ij}+\delta} = -\alpha_{ij} r^0_{ij} \left(\frac{\mathrm{d}^2\varphi_{ij}}{\mathrm{d}r^2_{ij}}\right)_{r^0_{ij}} \tag{33}$$

For systems with *Lennard-Jones* and electric dipole–dipole binary interactions one can obtain an analytical relationship between δ_{ij} and $\mathrm{d}\psi/\mathrm{d}r_{ij}$ in terms of parameters of these potentials. The derivative of the basic potential can be written as:

$$\frac{\mathrm{d}\varphi_{ij}}{\mathrm{d}r_{ij}} = -\frac{12\varepsilon_{ij}}{r_{ij}}\left\{\left(\frac{a_{ij}}{r_{ij}}\right)^{12} - \left(\frac{a_{ij}}{r_{ij}}\right)^{6} - \frac{\mu_i\mu_j}{4\varepsilon_{ij}a_{ij}^3}\left(\frac{a_{ij}}{r_{ij}}\right)^{3}\right\} \tag{34}$$

Or:

$$\frac{\mathrm{d}\varphi_{ij}}{\mathrm{d}r_{ij}} = -12\varepsilon_{ij}\left\{\frac{a_{ij}^{12}}{r_{ij}^{13}} - \frac{a_{ij}^{6}}{r_{ij}^{7}} - \frac{\mu_i\mu_j}{4\varepsilon_{ij}a_{ij}^3}\frac{a_{ij}^{3}}{r_{ij}^{4}}\right\} \tag{35}$$

The second derivative then is:

$$\frac{\mathrm{d}^2\varphi_{ij}}{\mathrm{d}r_{ij}^2} = \frac{12\varepsilon_{ij}}{r_{ij}^2}\left(\frac{a_{ij}}{r_{ij}}\right)^{3}\left\{13\left(\frac{a_{ij}}{r_{ij}}\right)^{9} - 7\left(\frac{a_{ij}}{r_{ij}}\right)^{3} - 4\frac{\mu_i\mu_j}{4\varepsilon_{ij}a_{ij}^3}\right\} \tag{36}$$

Separating the part that equals zero in the point of the minimum of potential ($r_{ij} = r_{ij}^0$) one obtains:

$$\frac{\mathrm{d}^2\varphi_{ij}}{\mathrm{d}r_{ij}^2} = \frac{12\varepsilon_{ij}}{r_{ij}^2}\left(\frac{a_{ij}}{r_{ij}}\right)^{3}\left\{9\left(\frac{a_{ij}}{r_{ij}}\right)^{9} - 3\left(\frac{a_{ij}}{r_{ij}}\right)^{3} + 4\left[\left(\frac{a_{ij}}{r_{ij}}\right)^{9} - \left(\frac{a_{ij}}{r_{ij}}\right)^{3} - \frac{\mu_i\mu_j}{4\varepsilon_{ij}a_{ij}^3}\right]\right\} \tag{37}$$

Second derivative in the point of the minimum of this potential is thus:

$$\left(\frac{\mathrm{d}^2\varphi_{ij}}{\mathrm{d}r_{ij}^2}\right)_{r_{ij}^0} = \frac{36\varepsilon_{ij}}{(r_{ij}^0)^2}\left(\frac{a_{ij}}{r_{ij}^0}\right)^{6}\left\{3\left(\frac{a_{ij}}{r_{ij}^0}\right)^{6} - 1\right\} \tag{38}$$

Deflections from the point of mechanical equilibrium due to the action of the many-body potential ψ are then given by:

$$\delta_{ij} = -\frac{(r_{ij}^0)^2}{36\varepsilon_{ij}}\frac{\left(\frac{\mathrm{d}\psi}{\mathrm{d}r_{ij}}\right)_{r_{ij}^0+\delta}}{\left(\frac{a_{ij}}{r_{ij}^0}\right)^{6}\left\{3\left(\frac{a_{ij}}{r_{ij}^0}\right)^{6} - 1\right\}} \qquad \alpha_{ij} = -\frac{r_{ij}^0}{36\varepsilon_{ij}}\frac{\left(\frac{\mathrm{d}\psi}{\mathrm{d}r_{ij}}\right)_{r_{ij}^0+\delta}}{\left(\frac{a_{ij}}{r_{ij}^0}\right)^{6}\left\{3\left(\frac{a_{ij}}{r_{ij}^0}\right)^{6} - 1\right\}} \tag{39}$$

On the other hand the gradient of the many-body potential can be expressed *via* parameters of the binary potential as:

$$\left(\frac{\mathrm{d}\psi}{\mathrm{d}r_{ij}}\right)_{r_{ij}^0+\delta} = -36\alpha_{ij}\frac{\varepsilon_{ij}}{r_{ij}^0}\left(\frac{a_{ij}}{r_{ij}^0}\right)^{6}\left\{3\left(\frac{a_{ij}}{r_{ij}^0}\right)^{6} - 1\right\} \tag{40}$$

At a first glance Eq. (40) does not involve parameters of the electric dipole–dipole interactions (μ_A, μ_B). In fact, information on these interactions is implicitly contained in the ratio a_{ij}/r_{ij}^0, differing from that of the pure *Lennard-Jones* potential $a_{ij}/r_{ij}^0 = 1$.

Triple interactions in configurations AAA, AAB, BAB, BBB, BBA, and ABA can be characterised by *variations of distances* r_{12} and r_{23}, arising from the action of the third molecule (Fig. 5). The deviation δ_{ij} is thus supposed to depend on the nature of the third molecule as reflected by the upper index to be used $\delta_{ij} = {\delta_{ij}}^k$, k denoting the nature of the third molecule (similarly ${\alpha_{ij}}^k = {\delta_{ij}}^k/r_{ij}$).

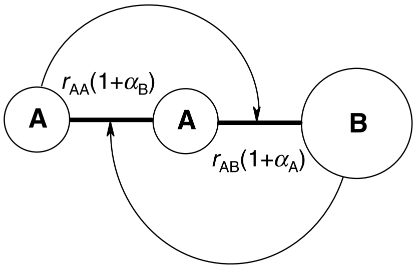

Fig. 5. The origin of the deflection of molecules from positions of mechanical equilibrium

From this point of view the gradient $d\psi_{AAB}/dr_{AB}$ in the configuration AAB arises from the action of the molecule A on the bond A–B and can be denoted as $G_{AB}{}^{A}$. The gradient $d\psi_{AAB}/dr_{AA}$ in the same configuration can be considered as originating from the action of the molecule B on the bond A–A; it can be denoted as $G_{AA}{}^{B}$. There are 6 such gradients and deflections that can be represented as $\delta_{AA}{}^{A} = r_{AA}\alpha_{AA}{}^{A}$, $\delta_{AB}{}^{A} = r_{AB}\alpha_{AB}{}^{A}$, $\delta_{BB}{}^{A} = r_{BB}\alpha_{BB}{}^{A}$, $\delta_{AA}{}^{B} = r_{AA}\alpha_{AA}{}^{B}$, $\delta_{AB}{}^{B} = r_{AB}\alpha_{AB}{}^{B}$, $\delta_{BB}{}^{B} = r_{BB}\alpha_{BB}{}^{B}$). The problem is thus strongly overparameterized: a given combination of ΔE_{ex}, Δ^{A}, and Δ^{B} can be achieved by a large number of combinations of gradients. One has to employ some regularization bounds.

It can be assumed that the *action* of the molecules A and B on the neighboring bond is of equal magnitude and opposite sign: $\alpha_{AA}{}^{B} = -\alpha_{AA}{}^{A}$, $\alpha_{BB}{}^{B} = -\alpha_{BB}{}^{A}$ (at complete equality $\alpha_{ij}{}^{B} = \alpha_{ij}{}^{A}$ the asymmetries are always zero). The action of molecules on hetero-molecular distances can be calculated according to the additivity rule: $\alpha_{AB} = 1/2(\alpha_{AA} + \alpha_{BB})$. This leaves us two adjustable parameters $\alpha_{AA}{}^{A}$ and $\alpha_{BB}{}^{A}$. The final regularization can be based on the assumption that the *reactions* of AA and BB bonds are also opposite: $\alpha_{AA}{}^{A} = -\alpha_{BB}{}^{A}$ (*i.e.* that the third molecule A increases the distance in the neighboring A–A pair but shortens it in the B–B pair).

Non-ideality parameters can be calculated for such systems in the following way. At first a_{ij} and r_{ij} are optimized for the minimum of chosen binary potentials as described in Ref. [9]. Then intermolecular distances are varied according to the values of $\alpha_{AA}{}^{A}$ (all other coefficients being computed *via* regularization bounds). This produces changes in energies of configurations that yield new non-ideality parameters whereas the gradient $G_{AA}{}^{A}$ is calculated according to Eq. (40). The dependences of ΔE_{ex}, Δ^{A}, and Δ^{B} on the gradient $G_{AA}{}^{A}$ are thus parametrically defined. The gradient $G_{AA}{}^{A}$ in this approximation is the only parameter of the three-center potential.

Under these conditions one obtains non-ideality parameters as polynomial functions of the gradient $G_{AA}{}^{A}$ (Table 2, Fig. 6). Negative gradient (positive $\alpha_{AA}{}^{A}$) yields positive asymmetries coupled to negative excess energy that can explain many cases of the two-step spin crossover. When the background excess energy is strongly positive (*e.g.* due to electric dipole–dipole interaction, Table 2) the variation of $G_{AA}{}^{A}$ brings about a wide spectrum of the shapes of transition curves from abrupt to the two-step spin crossover (Fig. 7).

The procedure described above can be inserted into a regression program allowing one to parameterize spin crossover transition curves in terms of ΔE^{0}, $T_{1/2}$, parameters of the *Lennard-Jones* potential, and coefficients $\alpha_{AA}{}^{A}$ and $\alpha_{BB}{}^{A}$.

Table 2. Non-idality parameters of a system of neutral complexes with a large contribution from electric dipole–dipole interactions ($\Delta E^0 = 14\,\mathrm{kJ/mol}$, $T_{1/2} = 155\,\mathrm{K}$, $\Delta\mu = 3\,\mathrm{D}$) and variable contribution of many-body interactions represented by the gradient $G_{AA}{}^{A}$; corresponding simulated curves are shown in Fig. 7

Fig. 7	$\alpha_{AA}{}^{A}$	$\frac{G_{AA}{}^{A}}{\mathrm{kJ/Å}}$	$\frac{\Delta E_{ex}}{\mathrm{kJ/mol}}$	$\frac{\Delta^{A}}{\mathrm{kJ/mol}}$	$\frac{\Delta^{B}}{\mathrm{kJ/mol}}$
1	0.000	0.0	7.152	0.000	0.000
2	0.016	−48.6	3.084	0.501	0.442
3	0.020	−60.8	0.954	0.981	0.866
4	0.026	−79.0	−2.938	2.163	1.909
5	0.028	−85.1	−4.406	2.706	2.388

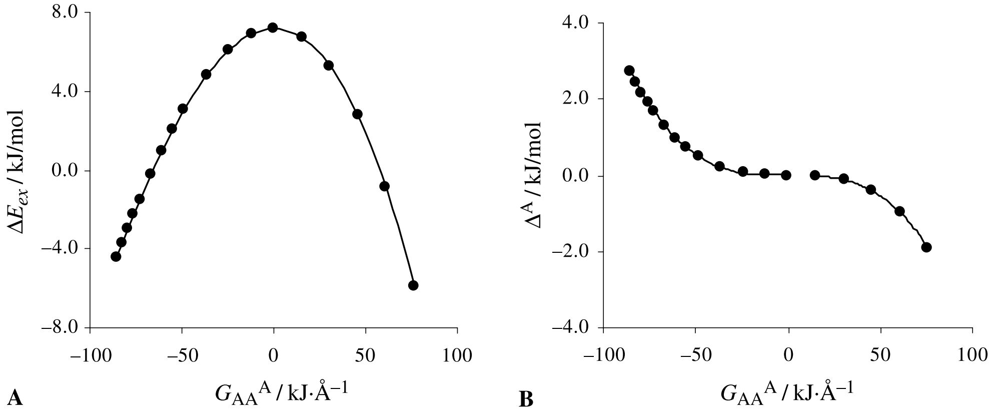

Fig. 6. Dependencies of non-ideality parameters on the gradient of many-body potential computed for a model system with a strong electric dipole–dipole contribution towards the excess energy ($\Delta E^0 = 14\,\mathrm{kJ/mol}$, $T_{1/2} = 155\,\mathrm{K}$, $\Delta\mu = 3\,\mathrm{D}$, see Table 2)

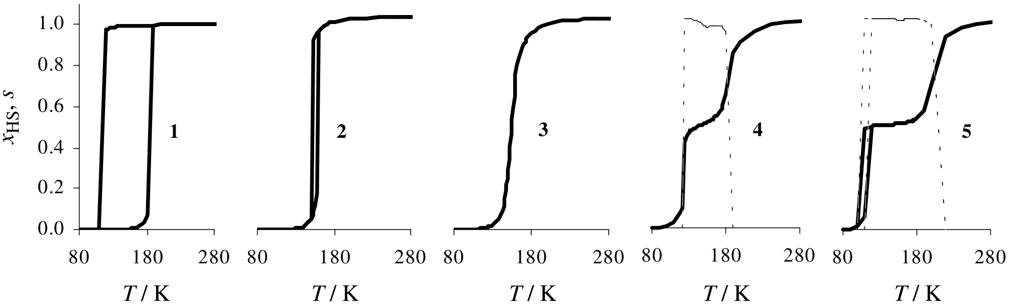

Fig. 7. Variations of the shape of transition curve caused by the variation of the gradient of many-body potential computed for a model system with parameters given in Table 2; dashed lines represent the degree of order

Figure 8 shows the results of such parameterization of the two-step spin crossover in $[\mathrm{Fe}(2\text{-}pic)_3]\mathrm{Cl}_2Et\mathrm{OH}$ (data from Ref. [16]). The standard energy of spin crossover was fixed at $\Delta E^0 = 6.14\,\mathrm{kJ/mol}$ according to calorimetric data [17]. The

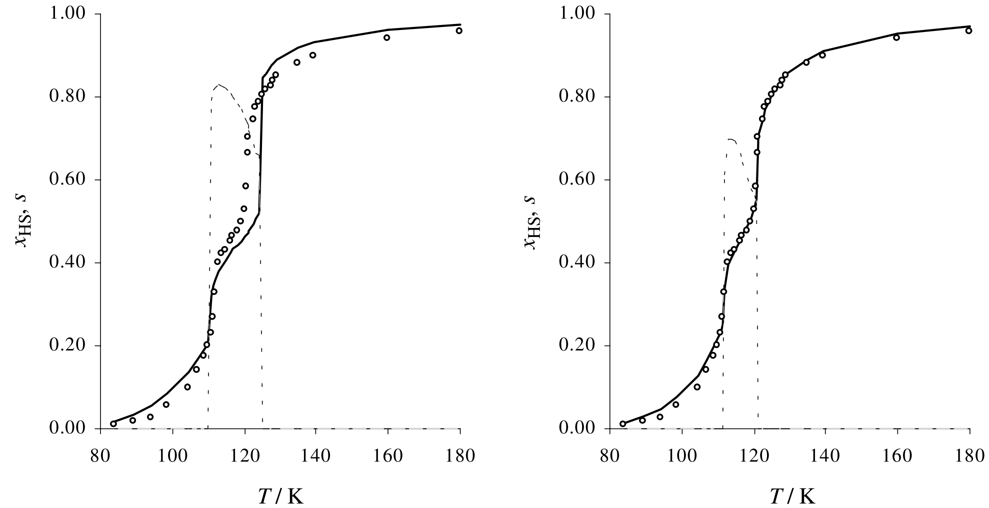

Fig. 8. Approximation of the data [13] on spin crossover in [Fe(2-*pic*)$_3$]Cl$_2$*Et*OH according to the model of triple interactions and ordering with triple interactions represented by relative deviations of molecular distances from those corresponding to the minima of binary potentials; parameters are given in Table 3; the left hand graph corresponds to the bound $\alpha_{AA}{}^{A} = -\alpha_{BB}{}^{A}$, the right hand graph was obtained by adjusting both $\alpha_{AA}{}^{A}$ and $\alpha_{BB}{}^{A}$. Dashed lines represent the degree of order

required distances r_{AA} and r_{BB} were assumed to equal the smallest lattice constants in LS and HS states of this compound according to Ref. [18]. The depth of the *Lennard-Jones* potential in the HS state was fixed at $\varepsilon_{BB} = 14\,\mathrm{kJ/mol}$, whereas ε_{AA} was considered as an adjustable parameter along with $T_{1/2}$, $\alpha_{AA}{}^{A}$, and $\alpha_{BB}{}^{A}$.

The regularization bound $\alpha_{AA}{}^{A} = -\alpha_{BB}{}^{A}$ has proven too strict for the parameterization of experimental transition curves, see Fig. 8A, first row in Table 3. The more flexible bound $\alpha_{AA}{}^{A} \approx -\alpha_{BB}{}^{A}$ allows one to adjust both these coefficients yielding an adequate description of the transition curve, Fig. 8B (second row in Table 3).

As has been shown above, the effect of the *Axilrod-Teller* potential in model spin crossover systems is small: it does not affect the excess energy and yields comparatively small asymmetries of splittings in compressed/expanded systems alone. Triple interactions of the *Axilrod-Teller* type thus only increase the sensi-

Table 3. Estimates of parameters obtained by fitting data [13] on spin crossover in [Fe(2-*pic*)$_3$]Cl$_2$*Et*OH according to the model of triple interactions and ordering with triple interactions represented by relative deviations of molecular distances from those corresponding to the minima of binary potentials ($\alpha_{AA}{}^{A}$ and $\alpha_{BB}{}^{A}$); binary interactions are represented by *Lennard-Jones* potential (ε_{ij}, a_{ij})

	σ_{yx}	ΔE^0 / kJ/mol	$T_{1/2}$ / K	$\alpha_{AA}{}^{A}$	$\alpha_{BB}{}^{A}$	ε_{AA} / kJ/mol	a_{AA} / Å	a_{BB} / Å	ΔE_{ex} / kJ/mol	Δ^{A} / kJ/mol	Δ^{B} / kJ/mol
$\alpha_{AA}{}^{A} = -\alpha_{BB}{}^{A}$	0.107	6.14	115.4 ± 0.7	0.0391 ± 0.0007	−0.0391	7.926 ± 0.125	11.3256	11.5710	−0.420	1.471	2.598
$\alpha_{AA}{}^{A} \approx -\alpha_{BB}{}^{A}$	0.015	6.14	115.5 ± 0.1	0.0403 ± 0.0001	−0.0368 ± 0.0001	8.019 ± 0.009	11.3256	11.5710	−0.354	1.630	2.151

tivity of a transition curve towards compression. The asymmetries corresponding to experimental shapes of spin crossover may arise from stronger many-body interactions, for example many-center exchange interactions. Such many-center potentials (of any type) can be taken into account *via* deviations of molecules from the points of mechanical equilibrium set by the known binary potential. In the approximation of small perturbations these deviations are proportional to the gradients of the many-center potentials. Dependencies of excess energies and asymmetries of splittings can be computed parametrically. Employing regularization bounds it is possible to achieve adequate parameterization of experimental transition curves of spin crossover in terms of parameters of *Lennard-Jones* potential and relative deviations of molecules from the position of mechanical equilibrium.

Methods

The minimisation of energy and calculations of non-ideality parameters have been achieved in Microsoft Excel$^{\text{TM}}$ worksheets employing the Solver tool. Regression of experimental data and simulation of transition curves have been performed using a multipurpose non-linear regression program OPTIMI supplied with the monograph, Ref. [19]. Details of regression procedure can be found in Refs. [6–9]. Transition curves are simulated (if not otherwise specified) for a model system characterized by $\Delta E^0 = 14\,\text{kJ/mol}$ and $T_{1/2} = \Delta E^0/\Delta S^0 = 155\,\text{K}$ that are independent of compression/expansion.

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