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Analytical solution of 1D Ising-like systems modified by weak long range interaction

Application to spin crossover compounds

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Abstract. It is well-known that 1D systems with only nearest neighbour interaction exhibit no phase transition. It is shown that the presence of a small long range interaction treated by the mean field approximation in addition to strong nearest neighbour interaction gives rise to hysteresis curves of large width. This situation is believed to exist in spin crossover systems where by the deformation of the spin changing molecules, an elastic coupling leads to a long range interaction, and strong bonding between the molecules in a chain compound leads to large values for nearest neighbour interaction constants. For this interaction scheme an analytical solution has been derived and the interplay between these two types of interaction is discussed on the basis of experimental data of the chain compound $[Fe(Htrz)_2(trz)](BF_4)_2$ which exhibits a very large hysteresis of 50 K above RT at 370 K. The width and shape of the hysteresis loop depend on the balance between long and short range interaction. For short range interaction energies much larger than the transition temperature k_BT_t the hysteresis width is determined by the long range interaction alone.

PACS. 64.30.+t Equations of state of specific substances – 64.60.Cn Order-disorder transformations; statistical mechanics of model systems

1 Introduction

Many features of thermal spin transition curves are reproduced by a free energy function which describes a solid solution of high spin (HS) and low spin (LS) molecules with an interaction term according to mean field theory. The population of the spin states of isolated non-interacting molecules as obtained in diluted mixed crystal systems follows the Boltzmann law so that the fraction of molecules in the HS state γ_H is determined by the partition functions $Z_\mathrm{HS}(T)$ and $Z_\mathrm{LS}(T)$, in which the energy levels of the HS states and LS states, respectively, are counted separately.

$$Z_Q(T) = \sum_i \exp(-\beta E_i^Q), \quad Q = \mathrm{HS}, \mathrm{LS}$$
$$\gamma_\mathrm{H} = \frac{Z_\mathrm{HS}(T)}{Z_\mathrm{HS}(T) + Z_\mathrm{LS}(T)} \tag{1}$$

where $\beta = k_\mathrm{B}T$ and k_B is the Boltzmann constant. Introducing the partial free energies $F_Q = -k_\mathrm{B}T\ln(Z_Q(T))$ of the pure HS and LS states, the thermal equilibrium of molecules in the HS and LS state are equivalently obtained from the minimum of the free energy expression for non-interacting molecules, $F_\mathrm{B}(\gamma_\mathrm{H}, T) = \gamma_\mathrm{H}F_\mathrm{HS}(T) + (1-\gamma_\mathrm{H})F_\mathrm{LS}(T) - TS_\mathrm{mix}$ with the mixing entropy $S_\mathrm{mix} = -k_\mathrm{B}[\gamma_\mathrm{H}\ln\gamma_\mathrm{H} + (1-\gamma_\mathrm{H})\ln(1-\gamma_\mathrm{H})]$.

The observed deviations from Boltzmann population in pure compounds has been accounted for by adding to F_B a term $W = \varDelta\gamma_\mathrm{H} - \varGamma\gamma_\mathrm{H}^2$,

$$F(\gamma_\mathrm{H}, T) = \gamma_\mathrm{H}F_\mathrm{HS}(T) + (1-\gamma_\mathrm{H})F_\mathrm{LS}(T) - TS_\mathrm{mix} + W \tag{2}$$

which can be considered as an expansion of $F = F_\mathrm{B} + W$ to second order in γ_H. This free energy first used by Drickamer *et al.* [1] explains the different steepnesses of the observed transition curves from gradual to abrupt transitions, and also hysteresis curves for sufficiently large values of $\varGamma$. $\varGamma$ has to be interpreted as an interaction constant describing the interaction between molecules in the HS state in mean field theory.

The interpretation of $\varGamma$ based on the properties of the spin changing molecules and their lattice has been one of the aims in spin crossover research. The increase of bond length of the molecules changing from LS to the HS state suggest, elastic interaction contributes to $\varGamma$ [2,3]. The observation by X-ray diffraction that the change of volume and shape of the crystal accompanying the spin

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transition is proportional to the HS fraction γ_{H} has given the impetus for a detailed evaluation of the contribution of the elastic interaction [4,5]. The spin changing molecules are considered as elastic dipoles in a homogeneous medium. The dipole strength can be calculated from the deformation tensor of the crystal changing the spin state and the elastic constants of the crystal. For the compound $[\mathrm{Fe}(2-\mathrm{pic})_3]\mathrm{Cl}_2 \cdot \mathrm{EtOH}$ the elastic contribution to the interaction constant was estimated to be of the size of the value used to fit the spin transition curve [5]. A typical bulk modulus of organometallic compounds was inserted. In case of the compound $[\mathrm{Fe(ptz)}_6](\mathrm{BF}_4)_2$ the elastic properties were measured by Brillouin spectroscopy [6]. In that case about 80% of the fitted interaction constant, that is $100\,\mathrm{cm}^{-1}$, has been calculated from the elastic dipole interaction. From these theoretical considerations and experimentally known properties of these types of compounds the elastic long range contribution seems to be limited to values less than $\Gamma < 200\,k_{\mathrm{B}}\,\mathrm{K}$. Using elasticity theory down to intermolecular distances in $[\mathrm{Fe(ptz)}_6](\mathrm{BF}_4)_2$ of 10 Å, elastic interaction energy differences of $30-40\,\mathrm{cm}^{-1}$ are calculated for the situation of two LS molecules, one of them changing to the HS state [7]. Short range interaction constants have been derived from thermal transition curves in $[\mathrm{Fe}_x\mathrm{Zn}_{1-x}(2\text{-pic})_3]\mathrm{Cl}_2\cdot$ EtOH exhibiting a two step transition [8] and the anomalous decay of the neat compound in the tunnelling region at 20 K [9]. Both phenomena could be well simulated with a short range interaction of antiferromagnetic type between two HS states of $-17\,\mathrm{cm}^{-1}$ which is less than the estimated values above.

Stronger short range interactions are expected for spin crossover compounds with a “direct” intermolecular bonding. A short range interaction constant of $-40\,\mathrm{cm}^{-1}$ was fitted to the two step thermal spin transition of binuclear compound [Fe(bt)(NCS)2]2bpym (bt = 2,2’-bi-2-thiazoline and bpym = 2,2’-bipyrimidine) [10]. Here the two iron ions are bridged by a bt ligand such that the spin state change of one of the iron ions may, by electron flow or by the displacement of the ligand as a result of the change of the bond length, directly influence the ligand field strength of the other iron ion.

The large hysteresis width of 50 K at 370 K observed for the compound $[\mathrm{Fe(Htrz)}_2(\mathrm{trz})](\mathrm{BF}_4)_2$ (Htrz= 1,2,4-4H-triazole; trz= 1,2,4-triazolato) [11] is beyond the widths which can be simulated on the basis of equation (2) with interaction constants as mentioned above. The basic structure of this material is a linear chain structure with octahedral Fe-$(\mathrm{Htrz})_6$ chromophores linked to each other through the 1, 2 nitrogen position of three triazole ligands [12]. The authors [12] raised the question whether there is an intimate relation between strong cooperativity and polymeric nature. First we state that short range (*i.e.* nearest neighbour) interactions do not lead to phase transitions independent of the size of the interaction. This statement is based on the well-known fact that the Hamiltonian (free energy) describing spin crossover systems can be mathematically mapped onto Ising systems [13–15] and that 1D systems do not order spontaneously if the interaction decreases faster than $J(k) = k^{-2}$ for the kth neighbour [16]. The key to understanding strong cooperativity may be long range elastic interactions which are present in any case and effectively introduce an interaction between the infinite chains. The study of this interaction scheme is the goal of this work.

2 Theoretical considerations

The interaction energy between two lattice sites at positions i and j in the crystal lattice may be expressed by terms $P_i A_{ij} P_j^\dagger$, where P and A are tensors. A_{ij} depends on the distance between sites i, j. In elasticity theory the second rank tensors P represent point defects and A_{ij} are fourth rank tensors. In a spin crossover system the deformation of the lattice accompanying the spin transition has been traced back to point defects at the iron ion of the spin changing molecule [4]. Elastic dipole tensors P^{H} and P^{L} have been attributed for the molecule in the HS and LS states, respectively. The interaction energy between all molecules is the double sum:

$$E_{\mathrm{I}} = \frac{1}{2}\sum_{i\neq j} P_i A_{ij} P_j^\dagger. \tag{3}$$

This sum implies that the tensors P^Q ($Q = \mathrm{HS}, \mathrm{LS}$) are independent of the spin state of the neighbouring molecules as already implied by the description as point defects embedded in an elastic medium. For crystals with one site per unit cell all tensors P^Q in the crystal are identical, the same principal values and the same orientation at each site. For short range interaction between molecules in a binuclear compound or a polymeric chain compound, where not only displacements give rise to energy shifts but also a redistribution of electrons within the common ligand of two spin changing iron atoms, the meaning of the tensors P and A may change. However, we will assume that still well defined quantities P^{H} and P^{L} can be attributed to atoms in the HS and LS state, respectively. Then this interaction energy can be expressed by operators σ_i with eigenvalues ± 1. With $P_i = (1/2)(P_i^{\mathrm{H}}(\sigma_i + 1) - P_i^{\mathrm{L}}(\sigma_i - 1))$, which gives back P_i^{H}, P_i^{L} for $\sigma_i = \pm 1$, respectively, the interaction sum consists of three terms:

$$\begin{aligned} E_{\mathrm{I}} = {} & \frac{1}{8}\sum_{i\neq j} \sigma_i \sigma_j P_i^{\mathrm{HL}} A_{ij} P_j^{\mathrm{HL}\dagger} \\ & + \frac{1}{4}\sum_{i\neq j} \sigma_i P_i^{\mathrm{HL}} A_{ij} (P_j^{H\dagger} + P_j^{\mathrm{L}\dagger}) \\ & + \frac{1}{8}\sum_{i\neq j} (P_i^{\mathrm{H}} + P_i^{\mathrm{L}}) A_{ij} (P_j^{H\dagger} + P_j^{\mathrm{L}\dagger}). \end{aligned} \tag{4}$$

In the first and second term enter the difference of the tensors $P^{\mathrm{HL}} = P^{\mathrm{H}} - P^{\mathrm{L}}$. For simplicity the unit cell of the lattice shall contain only one iron atom such that the subscripts i, j of the lattice sites can be omitted from the elastic dipole tensors. Then equation (4) can be simplified to

$$\begin{aligned} E_{\mathrm{I}} &= -\frac{1}{2}\sum_{i\neq j} J_{ij}\sigma_i\sigma_j + \sum_i \Delta_1\sigma_i + \Delta_2 \\ J_{ij} &= -\frac{1}{4}P^{\mathrm{HL}}A_{ij}P^{\mathrm{HL}\dagger} \\ \Delta_1 &= \frac{1}{4}NP^{\mathrm{HL}}\bar{A}(P^{H\dagger}+P^{\mathrm{L}\dagger}) \\ \Delta_2 &= \frac{1}{8}N^2(P^{\mathrm{H}}+P^{\mathrm{L}})\bar{A}(P^{H\dagger}+P^{\mathrm{L}\dagger}) \\ \bar{A} &= N^{-2}\sum_{i\neq j}A_{ij}. \end{aligned} \qquad (5)$$

With this notation the interaction energy between two sites is the same for HS-HS and LS-LS interaction, namely J_{ij}, and has the opposite sign for an interaction between HS and LS sites. This symmetry is obtained by the appropriate linear term $\Delta_1(\sigma_i+\sigma_j)$ and a constant energy shift Δ_2.

The Ising Hamiltonian for a chain compound of m chains and n atoms per chain can now be written down. If i_k is the index of an atom belonging to chain k, then the effective Hamiltonian H is given by:

$$\begin{aligned} H = \sum_k\sum_{i_k}\{&F^m_{\mathrm{HS}}(T)\frac{1}{2}(\sigma_{i_k}+1) - F^m_{\mathrm{LS}}(T)\frac{1}{2}(\sigma_{i_k}-1) \\ &+\Delta_1\sigma_{i_k}\} - \frac{1}{2}\sum_{k,k'}\sum_{i_k\neq j_{k'}} J_{i_k j_{k'}}\sigma_{i_k}\sigma_{j_{k'}} + m\Delta_2. \end{aligned} \qquad (6)$$

The Hamiltonian is called effective because the Hamiltonian of the atom i_k with infinite numbers of eigenvalues belonging to the HS and LS state of the atom is replaced by their free energies. This is possible as the full partition function can be partially carried out [15], namely $Z^m_{\mathrm{HS}}(T)$ and $Z^m_{\mathrm{LS}}(T)$, and their free energies included in an effective two state Hamiltonian. In a next step, the interaction term is split up for short range interaction within the chains and long range interaction between all atoms, which is treated in mean field approximation by replacing $\sigma_{j_{k'}}$ by its mean value $\langle\sigma\rangle$. Omitting constant energy terms and denoting $\Delta F^m_{\mathrm{HL}} = F^m_{\mathrm{HS}} - F^m_{\mathrm{LS}}$ equation (6) becomes:

$$\begin{aligned} H = \sum_k\sum_{i_k}&\frac{1}{2}(\Delta F^m_{\mathrm{HL}}(T) + 2\Delta_1 \\ &-\sum_{k' j_{k'}} J^{\mathrm{e}}_{i_k j_{k'}}\langle\sigma\rangle)\sigma_{i_k} \\ &-\frac{1}{2}\sum_k\sum_{i_k j^n_k} J^{\mathrm{c}}_{i_k j^n_k}\sigma_{i_k}\sigma_{j^n_k}. \end{aligned} \qquad (7)$$

The index j^n_k runs over the two neighbours in a chain. The interaction constant inside the chain has the superscript c. It shall be the same for the two neighbours such that $J^{\mathrm{c}} = J^{\mathrm{c}}_{i_k j^n_k}$ does not depend on the site. The superscript e stands for the elastic long range interaction in the double sum $\sum_{k' j_{k'}} J^{\mathrm{e}}_{i_k j_{k'}}$ which is also independent of the index i_k, because all sites i_k shall be equivalent. It is replaced by its average: $nm\bar{J}^{\mathrm{e}}$. The linear term in σ_i does not depend on any index and can therefore be treated as a field B acting on each site. The contribution $(1/2)nm\bar{J}^{\mathrm{e}}\langle\sigma\rangle$ is the mean field of the elastic long range interaction

$$B(T,\langle\sigma\rangle) = -\frac{1}{2}(\Delta F^m_{\mathrm{HL}}(T) + 2\Delta_1 - nm\bar{J}^{\mathrm{e}}\langle\sigma\rangle). \qquad (8)$$

When inserting $B(T,\langle\sigma\rangle)$ into equation (7) one recognises that the Hamiltonian can be written as a sum $\sum_k^m H_k$ of m independent Hamiltonians H_k of infinite chains in an applied field of energy $B\sigma_i$

$$H_k = -J^{\mathrm{c}}\sum_{i_k}^n \sigma_{i_k}\sigma_{i_k+1} - B\sum_{i_k}^n \sigma_{i_k}. \qquad (9)$$

The well-known closed analytical solution for the free energy of H_k obtained by the transfer matrix method and its derivative is given by [16]

$$\begin{aligned} F_k(T,B) = -k_{\mathrm{B}}T\ln\{&\mathrm{e}^{\beta J^{\mathrm{c}}}\cosh(\beta B) \\ &+[\mathrm{e}^{2\beta J^{\mathrm{c}}}\sinh^2(\beta B) + \mathrm{e}^{-2\beta J^{\mathrm{c}}}]^{\frac{1}{2}}\} \end{aligned}$$

$$\begin{aligned} \left\langle \sum_{i_k}^n \sigma_{i_k} \right\rangle &= \frac{\partial}{\partial B}\left(-\frac{F_k(B,T)}{k_{\mathrm{B}}T}\right) \\ &= \frac{\sinh(\beta B)}{[\sinh^2(\beta B) + \mathrm{e}^{-4\beta J^{\mathrm{c}}}]^{\frac{1}{2}}}\cdot \end{aligned} \qquad (10)$$

Inserting B from equation (8) this equation (10) represents an implicit equation for the expectation value $\langle\sigma\rangle = \langle\sum_{i_k}^n \sigma_{i_k}\rangle$. In the limit of $J^{\mathrm{c}} = 0$ the implicit equation is obtained when derived from the mean field free energy equation (2) with the HS fraction $\gamma_{\mathrm{H}} = (\langle\sigma\rangle+1)/2$ as order parameter. Comparison of the coefficients give the relations between the interaction constants and energy shifts of both representations

$$\Gamma = nmJ^{\mathrm{e}} \qquad \text{and} \qquad \Delta = 2\Delta_1 + nmJ^{\mathrm{e}}. \qquad (11)$$

The opposite limit of infinite interaction J^{c} inside the chain reduces the implicit equation to

$$\langle\sigma\rangle = \frac{\sinh(\beta B)}{\sqrt{\sinh^2(\beta B)}}\cdot \qquad (12)$$

The solution is $\langle\sigma\rangle = \pm 1$ with the change of sign at $B(\langle\sigma\rangle,T) = 0$. The two temperatures for $\langle\sigma\rangle = \pm 1$ define the widths of the hysteresis for this limit. Expanding $\Delta F^m(T)$ the condition reads

$$\Delta F^m_{\mathrm{HL}}(T_{\mathrm{t}}) - \Delta S^m_{\mathrm{HL}}(T_{\mathrm{t}})(T - T_{\mathrm{t}}) + 2\Delta_1 - \Gamma\langle\sigma\rangle = 0 \qquad (13)$$

where $-\Delta S^m$ is inserted for the derivative $\partial F^m/\partial T$. For $\langle\sigma\rangle = \pm 1$, this condition determines the temperatures $T^{\downarrow}$ and $T^{\uparrow}$, respectively, so that the hysteresis widths $\Delta T = T^{\uparrow} - T^{\downarrow}$ depend only on the infinite range interaction and the molecular entropy change at temperature T_{t}

$$\Delta T = \frac{2\Gamma}{\Delta S^m_{\mathrm{HL}}(T_{\mathrm{t}})}\cdot \qquad (14)$$

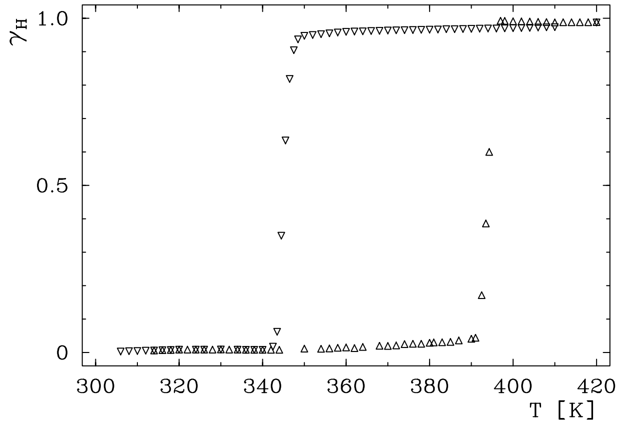

Fig. 1. HS fraction γ_{H} *versus* temperature T in the warming ($\triangle$) and cooling mode ($\bigtriangledown$) for the chain compound $[\mathrm{Fe(Htrz)_2(trz)}](\mathrm{BF_4})$.

As with increasing interaction constants hysteresis widths are increasing, the above value represents an upper limit for a fixed infinite range interaction constant Γ.

Finally the total enthalpy and entropy difference at a temperature T_{t} between the system in the HS and the LS state are given in order to compare with thermodynamic data. In the limit of infinite intra-chain interaction $J^{\mathrm{c}} = \infty$ the interaction parameter does not enter the expressions. As in mean field theory the simple relation between molecular properties $\Delta H^m_{\mathrm{HL}}, \Delta S^m_{\mathrm{HL}}$ of noninteracting molecules and $\Delta H_{\mathrm{HL}}, \Delta S_{\mathrm{HL}}$ of the interacting system are obtained

$$\begin{aligned} \Delta S(T_{\mathrm{t}}) &= \Delta S^m_{\mathrm{HL}}(T_{\mathrm{t}}) \\ \Delta H(T_{\mathrm{t}}) &= \Delta S^m_{\mathrm{HL}}(T_{\mathrm{t}})T_{\mathrm{t}}. \end{aligned} \tag{15}$$

$\Delta H_{\mathrm{HL}}, \Delta S_{\mathrm{HL}}$ in this context are also understood as quantities per molecule.

3 Discussion

The spin transition curve of the chain compound $[\mathrm{Fe(Htrz)_2(trz)}](\mathrm{BF_4})_2$ derived from susceptibility data [11] is shown in Figure 1. The large hysteresis width of $\Delta T = T^{\uparrow} - T^{\downarrow} = 50$ K at a high transition temperature $T_{\mathrm{t}} = (T^{\uparrow} + T^{\downarrow})/2 = 370$ K, when simulated in mean field theory (Eq. (2)), requires an interaction parameter $\Gamma/k_{\mathrm{B}} = 1330$ K (Fig. 2) which is far beyond the contribution expected from elasticity theory.

The simulated S-shaped curve $\gamma_{\mathrm{H}}(T)$ in Figure 2 represents the extrema of the free energy. The transition temperatures are given by the infinite slopes of $\gamma_{\mathrm{H}}(T)$. The free energy is completely defined by the difference of the molecular entropies $\Delta S^m_{\mathrm{HL}}(T_{\mathrm{t}})$, the temperature T_{t} and the interaction constants. Using the specific heat data [11] of the compound the molecular entropy difference derived from the large enthalpy change of $27\,\mathrm{kJ\,mol^{-1}}$ according to equation (15) amounts to $12.18\,k_{\mathrm{B}}$. In the two cases of mean field limit ($J^{\mathrm{c}} = 0$) and strong chain interaction limit($J^{\mathrm{c}} = \infty$) equation (15) is valid. For the range of parameters under discussion $\Delta S_{\mathrm{HL}}(T_{\mathrm{t}})$ of the system has been calculated numerically and deviated only by few %, so that the value of $12.18\,k_{\mathrm{B}}$ for $\Delta S^m_{\mathrm{HL}}(T_{\mathrm{t}})$ is used throughout.

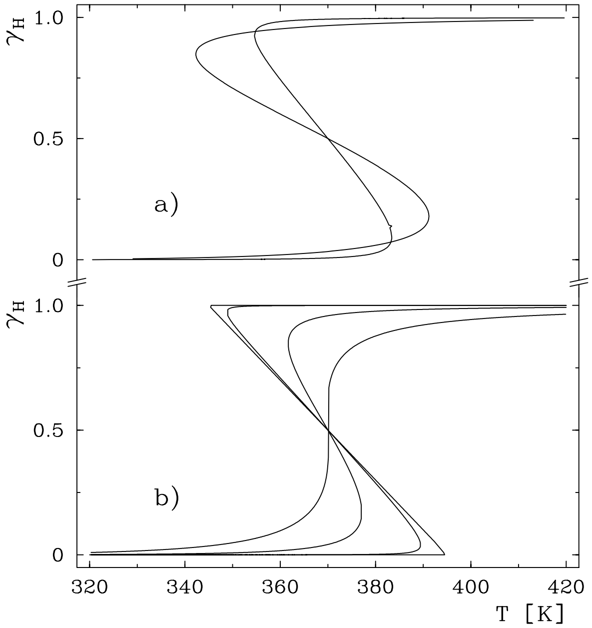

Fig. 2. The HS fraction $\gamma_{\mathrm{H}} = (\langle\sigma\rangle + 1)/2$ which minimizes or maximizes the free energy for a chain compound is plotted *versus* temperature T. (a) The S-shaped curve which leads to a hysteresis width of 50 K is calculated in mean field approximation with $\Gamma/k_{\mathrm{B}} = 1330$ K and the second curve with $\Gamma/k_{\mathrm{B}} = 210$ K and $J^{\mathrm{c}}/k_{\mathrm{B}} = 560$ K (see text). (b) Curves with increasing intra-chain interaction constants $J^{\mathrm{c}}/k_{\mathrm{B}} = 240$, 400, 800, 2000 K and a fixed mean field long range interaction constant $\Gamma/k_{\mathrm{B}} = 210$ K are shown for comparison of the shapes. $J^{\mathrm{c}}/k_{\mathrm{B}} = 240$ K is the limit for a hysteresis transition. The curves become S-shaped for larger values of J^{c}. For $J^{\mathrm{c}}/k_{\mathrm{B}} = 2000$ K the curve is almost Z-shaped and represents the limit $J^{\mathrm{c}} = \infty$.

Comparing the shape of the experimental transition curve and simulated S-shaped curve in Figure 2a with $\Delta T = 50$ K the curvatures at temperatures $T \geq T^{\downarrow}$ and $T \leq T^{\uparrow}$ are much more pronounced for the S-shaped curve. The abruptness of the transitions obviously cannot be obtained in mean field theory. Figure 2b shows solutions of equation (10) for different values J^{c} of the intra-chain interaction and a fixed value $\Gamma/k_{\mathrm{B}} = 210$ K for the long range interaction treated in mean field approximation. This value has been calculated from equation 14 inserting $\Delta T = 50$ K and the $\Delta S^m_{\mathrm{HL}}(T_{\mathrm{t}})$ value from above, so that $\Gamma/k_{\mathrm{B}} = 210$ K has to be considered as a lower limit for the long range contribution, which gives the hysteresis width of $\Delta T = 50$ K in case of very large intra chain interaction. For $J^{\mathrm{c}}/k_{\mathrm{B}} = 2000$ K a Z-shaped curve is calculated meaning that the curvatures at temperatures $T \geq T^{\downarrow}$ and $T \leq T^{\uparrow}$ are vanishing. With decreasing J^{c} the hysteresis width decreases, the curvatures are increasing, and for $J^{\mathrm{c}}/k_{\mathrm{B}} = 240$ K the hysteresis vanishes.

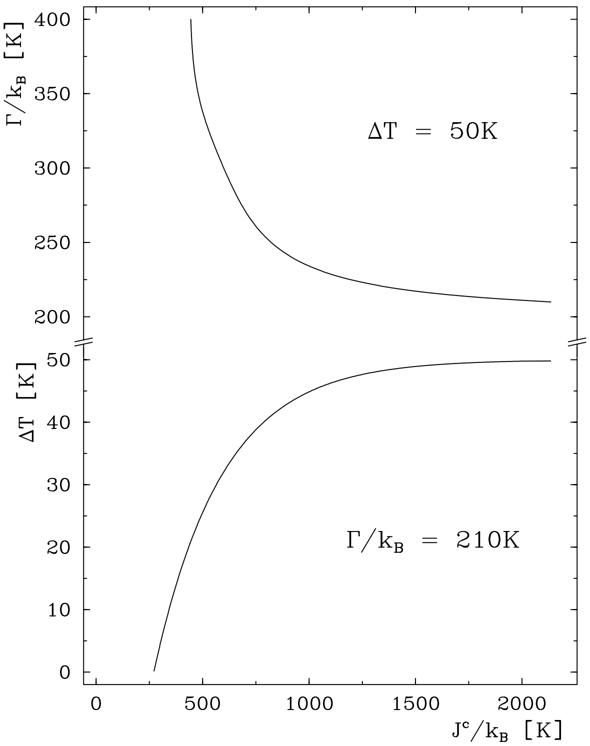

Fig. 3. With the measured values of molecular entropy difference $\Delta S_{\mathrm{HL}}^{m}(T_{\mathrm{t}})$ and the transition temperature $T_{\mathrm{t}} = 370$ K the interaction constant Γ is plotted *versus* the intra-chain interaction J^{c} as necessary for the observed hysteresis widths of 50 K in the upper curve. The lower curve shows the dependency of the hysteresis width on the intra-chain interaction J^{c} at constant $\Gamma/k_{\mathrm{B}} = 210$ K.

The experimental transition curve with its small curvatures seems to be close to the limiting case such that the value of Γ is close to its lower limit and J^{c} is very large, of the order of 1000 K. In Figure 3 the pairs of values Γ *versus* J^{c} for the measured hysteresis widths are plotted. The lower limit $\Gamma = 145\,\mathrm{cm}^{-1}$ is of the size which has been estimated for the compound $[\mathrm{Fe}(2-\mathrm{pic})_3]\mathrm{Cl}_2\cdot\mathrm{EtOH}$ [5]. Much higher values are not expected on the basis of elasticity theory. Consequently a very large intra-chain interaction is required in the present interaction scheme. Whether such large nearest neighbour interactions by ligand bridged iron atoms are realistic is an open question, but there must be large interactions as is obvious from the mean field approximation.

The following argument may support this view. As any interaction scheme can be treated in the mean field approximation, the mean field approximation of equation (9) shall be considered. The total mean field interaction value is $\Gamma_m = \Gamma + 2J^{\mathrm{c}}$ where the factor 2 stems from two nearest neighbours. $\Gamma_m/k_{\mathrm{B}} = 1330$ K fits the hysteresis width of 50 K. Γ/k_{B} fixed to the lower limit of 210 K an intra-chain interaction of $J^{\mathrm{c}}/k_{\mathrm{B}} = (1330\,\mathrm{K} - 210\,\mathrm{K})/2$ is needed in the mean field approximation. This value however does not reproduce the widths of 50 K in the exact calculation as is shown in Figure 2a by the narrower S-shaped curve. This means that the mean field approximation underestimates the interactions.

In Figure 3 the hysteresis width versus intra-chain interaction with fixed Γ is also plotted. At $J^{\mathrm{c}}/k_{\mathrm{B}} = 240$ K the width vanishes and at lower values the transition becomes more and more gradual.

Summarising the situation we are faced with, the interaction scheme of strong intra-chain interaction and long range interaction between all spin crossover molecules requires on the one hand long range interaction constants which are in the range of the contributions from elastic interactions, and on the other hand very large short range nearest neighbour interaction of the order of $1000\,\mathrm{cm}^{-1}$ inside the chain.

The interplay between long range and strong short range interaction of layer compounds shall be explored by Monte-Carlo simulation in a future work.

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