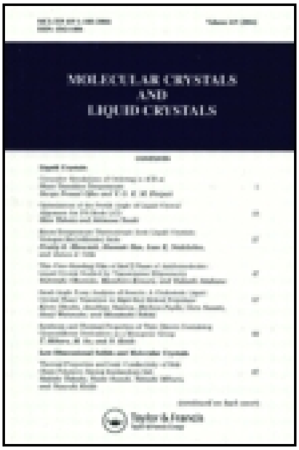

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Two-Level Models for the Two-Step Spin Crossovers

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TWO-LEVEL MODELS FOR THE TWO-STEP SPIN CROSSOVERS

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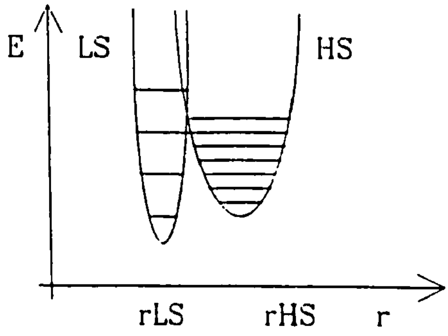
Abstract We discuss here the physical bases of discrete models for the spin crossover systems, and we consider specifically the case of two sublattices which reproduces the so-called *two-step transitions.*

INTRODUCTION

The spin crossover phenomenon is now well understood at the intramolecular level [1]: the configurational diagram (Fig.1) is made of two weakly coupled curves of parabolic shape, each of them corresponding to a spin state of the metallic complex. The low (resp. high) spin state has lower (resp. higher) energy value, smaller (resp. larger) metal-ligand distance, and higher (resp. lower) vibrational frequency. The increase in metal-ligand distance upon LS ⇌ HS conversion is explained by the population of antibonding orbitals (e_g in octahedral symmetry). This distance increase is particularly large in the case of Fe^{II} (0.02 A), since two electrons move from t_{2g} to e_g orbitals.

Fig 1 Configurational diagram of the spin crossover : adiabatic potential vs metal-ligand distance, and vibrational levels in the Born -Oppenheimer approach



Several models based on interacting two-level systems have been proposed several years ago [2,3]. It is possible now to relate the two-level structure and the vibronic scheme of Fig.1:

(i) for vibrations such as metal-ligand stretching (which actually derive from the adiabatic potential of Fig.1), $\hbar\omega \gtrsim kT$, so that only the vibrational groundstate of each electronic state is sizably populated. This leads to a two-level scheme whose energy difference depends on the vibrational frequencies $\omega_{LS} \neq \omega_{HS}$ (this enables explaining the isotopic effect [4]).

(ii) for low-frequency intramolecular vibrations, $\hbar\omega \ll kT$, the vibrational contributions to the partition function factorize, and the vibronic scheme -except for a temperature-dependent energy shift- is equivalent to a two-level system whose degeneracy ratio accounts for both electronic and vibrational effects.

We have also considered the effect of a thermal shift of the energy levels ($\Delta = \Delta_0 - \gamma T$). This only results in multiplicative factors to the degeneracies, whose ratio is multiplied by $\exp(\frac{\gamma}{k_B})$. So, the two-level description implies an **effective degeneracy ratio:**

$$r_{eff} = \frac{g^{el}_{HS}}{g^{el}_{LS}} \cdot \frac{\omega_{LS}}{\omega_{HS}} \cdot \exp(\frac{\gamma}{k_B T})$$

which includes electronic, vibrational and thermal expansion effects. This effective ratio is related to the change of the molar entropy upon conversion:

$$\Delta S = k \operatorname{Ln} r_{eff}$$

Experimental data concerning both ΔS and the high-temperature values of $n_{HS}(T)$ require rather large values of r_{eff}, in large excess of the spin-only value 5 for Fe^{II} (the orbital moment is usually quenched and can be neglected). The role of the vibrations in the spin crossover will be described in greater detail in a forthcoming paper.

For modelizing the solid-state properties, the coupled two-level systems are described by the following hamiltonian (after [2,3], whose equivalence is shown in [5]):

$$\hat{\mathcal{H}} = \sum_i \frac{\Delta}{2} < \hat{\sigma}_i > + \sum_{<i,j>} J_{ij} <\hat{\sigma}_i><\hat{\sigma}_j> \qquad \text{(eq.1)}$$

where $\hat{\sigma}_i$ is a fictitious spin with eigenvalues $\sigma = -1$ (low spin) and $\sigma = +1$ (high spin). Then $n_{HS}(T) = (<\hat{\sigma}> + 1)/2$.

Eq.1 formally describes an Ising-like system under external field (Δ); the suffix *like* denotes that, at variance from magnetic systems, the degeneracies of the two levels are not the same. The mean-field treatment of eq.1 leads to the single molecule hamiltonian:

$$\hat{\mathcal{H}} = \frac{\Delta}{2}\,\hat{\sigma} + J <\hat{\sigma}>\hat{\sigma} \qquad \text{(eq.2)}$$

whose eigenvalues are:

$$E(+1) = \frac{\Delta}{2} + J <\hat{\sigma}>$$

$$E(-1) = -\frac{\Delta}{2} - J <\hat{\sigma}>$$

Thus the energy distance between the twolevels linearly depends on the high-spin ratio. Such a linear dependence was postulated in both previous papers [2,3], and now can bejustified ***a posteriori*** by the elegant experiments of Light Induced Excited Spin State Trapping (LIESST [6]), which show that the height ΔE_B of the energy barrier in the configurational diagram varies quasi-linearly with n_{HS} at constant temperature: the observed **increase** of ΔE_B vs n_{HS} can be associated, considering a simple shift of the HS and LS curves, with a **decrease** in the energy difference $E_{HS} - E_{LS}$; this is precisely what the two-level model yields with a negative ("ferromagnetic") J-value.

We focus here on the application of the two-level model to two-sublattices systems. We recently published [7] a full mean-field treatment of the problem, where the combination of a "*ferro*-magnetic" *intra*-sublattice ($J<0$) and "*antiferro*-magnetic" *inter*-sublattice ($J_{AB}>0$) led to a "two-step" conversion curve. The one-site hamiltonians for the sublattices are:

$$\hat{\mathcal{H}}_A = \frac{\Delta}{2} \cdot \hat{\sigma}_A + \hat{\sigma}_A \left[J_A \left\langle \hat{\sigma}_A \right\rangle + J_{AB} \left\langle \hat{\sigma}_B \right\rangle\right]$$
$$\hat{\mathcal{H}}_B = \frac{\Delta}{2} \cdot \hat{\sigma}_B + \hat{\sigma}_B \left[J_B \left\langle \hat{\sigma}_B \right\rangle + J_{AB} \left\langle \hat{\sigma}_A \right\rangle\right] \qquad \text{(eq.3)}$$

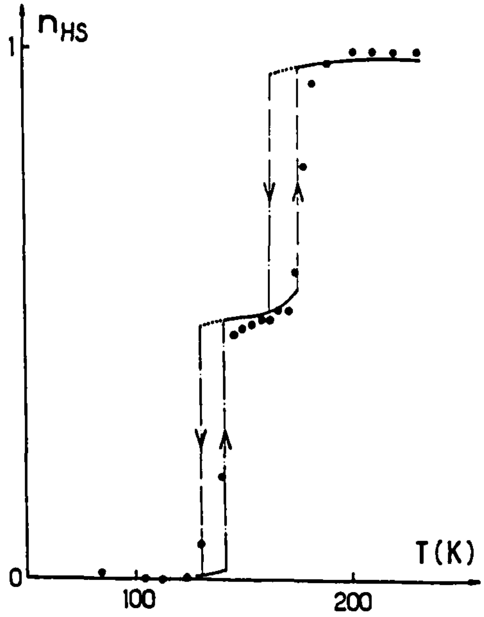


Fig.2 Experimental data of $Fe^{II}[5NO_2\text{-sal-}(1,4,7,10)]$, from [8], fitted with: Δ = 920 K, J = -280 K, J_{AB} = 29 K, r_{eff} = 400.

The mechanism responsible for the two-step evolution is the antiferromagnetic interaction which slows down the spin conversion of either sublattice when the other undergoes its spin conversion. Interesting features of the model have been developed in [7]: spontaneous symmetry breaking in a temperature range limited by two "Néel temperatures", first order transition associated with a simultaneous reversal of the "magnetizations" of the sublattices when these are structurally unequivalent. Experimental data fitted with the full mean-field model are shown in Fig.2.

A particularly interesting case is that of the "bimetallic" complex $[Fe(bt)(NCS)_2]_2bpym$ [9], whose Mössbauer study strongly suggests that the antiferromagnetic interaction is of intramolecular origin. For this case, we have adapted the mean-field treatment by resolving the single molecule hamiltonian (which describes a pair of coupled two-level systems):

$$\hat{\mathfrak{H}}_p = \frac{\Delta}{2}\left(\hat{\sigma}_A + \hat{\sigma}_B\right) + J\left(\hat{\sigma}_A\left\langle\hat{\sigma}_A\right\rangle + \hat{\sigma}_B\left\langle\hat{\sigma}_B\right\rangle\right) + J_{AB}\,\hat{\sigma}_A\cdot\hat{\sigma}_B \qquad \text{(eq.4)}$$

this modified mean-field treatment is similar to that introduced by Oguchi [10] in magnetism to account for correlations in the ferromagnetic problem. A detailed description will be given in [11]. To summarize, the main features concerning $n_{HS}(T)$ are qualitatively similar to those of the full mean-field treatment, except that the two sublattices are now quantum-mechanically indistinguishable. A fit of the experimental $n_{HS}(T)$ is reported in Fig.3; the calculated value of the entropy change per metallic ion, 44 J K^{-1} $mole^{-1}$, is in excellent agreement with the measured value, 41 ± 3 J K^{-1} $mole^{-1}$ [9].

CONCLUSION

Two-level models can include all essential ingredients of the spin crossover conversion: electronic and vibrational. They enable reproducing the various shapes of the experimental conversion curves.

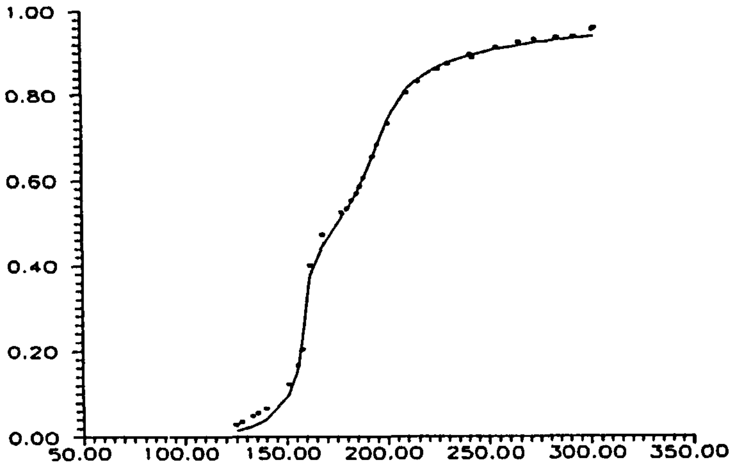


Fig.3 Best fit of the conversion curve [9] of $[Fe(bt)(NCS)_2]_2bpym$, with: Δ = 778 K, J = - 283 K, r_{eff} = 84.

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