Dynamical Ising-like model for the two-step spin-crossover systems

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In order to reproduce the two-step relaxation observed experimentally in spin-crossover systems, we investigate analytically the static and the dynamic properties of a two-sublattice Ising-like Hamiltonian. The formalism is based on a stochastic master equation approach. It is solved in the mean-field approximation, and yields two coupled differential equations that correspond to the HS fractions of the sublattices A and B. © *2003 American Institute of Physics.*
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I. INTRODUCTION

Recently a new spin-crossover $(SC)^{1,2}$ compound {Fe(pmd) [Ag(CN)$_2$] [Ag$_2$(CN)$_3$]} that shows a thermal double step transition has been synthetized.[3] We report here on the relaxation behavior of the nonequilibrium photoinduced high-spin state. A strong nonlinear character of the relaxation curve has been observed: two regimes are obtained, reminiscent of the associated equilibrium double step character.

To explain this behavior, we propose a microscopic dynamical model for a two sublattice system that takes into account two interaction parameters: a "ferromagnetic" intrasublattice (J_1) and a "antiferromagnetic" intersublattice (J_2).

II. ISING-LIKE MODEL FOR THE TWO-STEP SPIN TRANSITION

The spin Hamiltonian that describes the two-step SC transitions can be written in the form of the Ising Hamiltonian of a ferrimagnetic system.[2] We denote by A and B the two sublattices.

Associated with these two quantities are the following fictitious two-state operators s^A and s^B for which eigenvalues -1 and $+1$ correspond, respectively, to the LS and the HS states.

For the present model, the Hamiltonian of the system is written as

$$H = -J_1 \sum_{\langle i,j\rangle} s_i^A s_j^A - J_1 \sum_{\langle i,j\rangle} s_i^B s_j^B - J_2 \sum_{\langle i,j\rangle} s_i^A s_j^B$$
$$+ \left(\frac{\Delta}{2} - \frac{kT}{2}\ln g\right)\sum_i (s_i^A + s_i^B), \quad (1)$$

where Δ and g are the ligand field energy and the degeneracy. J_1 and J_2 are coupling parameters with the following signs: $J_1 > 0$ (ferro) and $J_2 < 0$ (antiferro). We will assume in the rest of this work that the intensities of the interactions

between pairs $A-A$, $B-B$, and $A-B$ are independent of their position in the lattice. In the mean-field approach, the one site Hamiltonian becomes

$$H_i^{CM} = -s_i^A\left(J_2\langle s_B\rangle + J_1\langle s_A\rangle - \frac{\Delta}{2} + \frac{kT}{2}\ln g\right)$$
$$-s_i^B\left(J_2\langle s_A\rangle + J_1\langle s_B\rangle - \frac{\Delta}{2} + \frac{kT}{2}\ln g\right), \quad (2)$$

where J_1 and J_2 include the contributions of the coordination number z. Self-consistent equations are then obtained through the average values $\langle s_A\rangle = \mathrm{tr}(s_A e^{-\beta H_i})$ and $\langle s_B\rangle = \mathrm{tr}(s_B e^{-\beta H_i})$ giving the following system of coupled nonlinear equations:

$$\langle s_A\rangle = \tanh X, \quad \langle s_B\rangle = \tanh Y, \quad (3)$$

with

$$X = \beta\left(J_2\langle s_B\rangle + J_1\langle s_A\rangle - \frac{\Delta}{2} + \frac{kT}{2}\ln g\right);$$
$$Y = \beta\left(J_2\langle s_A\rangle + J_1\langle s_B\rangle - \frac{\Delta}{2} + \frac{kT}{2}\ln g\right). \quad (4)$$

The static (thermodynamical equilibrium) version of this model has been well studied in the past by Bousseksou *et al.*[2] It is quite easy to demonstrate that this system reproduces the thermal double step SC transitions observed in Mössbauer and magnetic experiments. These two transitions are in fact due to the two sublattices which make the spin transition at different temperatures because of the antiferroelastic coupling which breaks the symmetry at the transition. Let us denote by T_{e1} and T_{e2} the two transition temperatures responsible for the existence of a plateau. These two temperatures can cancel the effective field acting on each sublattice, which gives the following relations defining T_{e1} and T_{e2}:

$$\frac{\Delta}{2} - \frac{kT_{e1}}{2}\ln g + J_2 m_B(T_{e1}) = 0,$$
$$\frac{\Delta}{2} - \frac{kT_{e2}}{2}\ln g + J_2 m_A(T_{e2}) = 0. \quad (5)$$

It is straightforward that if we put $J_2 = 0$ (no antiferroelastic coupling), we obtain immediately two equivalent sublattices

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with the same transition temperature $T_{e0} = \Delta/k_B \ln g$. To have a two-sublattice system in the low spin state at 0 K, we must consider the following condition:

$$J_2 < J_1 + \frac{\Delta}{2}. \tag{6}$$

It is also interesting to note that T_{e1} and T_{e2} can be approximated well by the following analytical formulas:

$$T_{e1} \cong \frac{\Delta - 2|J_2|}{k_B \ln g} \quad \text{and} \quad T_{e2} \cong \frac{\Delta + 2|J_2|}{k_B \ln g}. \tag{7}$$

It follows that the width of the plateau is given by $\delta T_e \cong 4|J_2|/k_B \ln g$. The latter is directly proportional to antiferroelastic coupling J_2.

III. DYNAMICAL ASPECTS

The dynamical properties[4] of the adapted Ising-like model for the two-step spin crossover system is studied in the general stochastic formalism of the master equation introduced by Glauber.[5] The latter is based on the simple idea that each individual site interacts with a thermal bath which changes its state randomly over time. In the present case, the thermal bath spontaneously induces spin flip of the fictitious spins from $s^A(s^B)$ to $-s^A(-s^B)$.

Let us denote by $W_j(s_1^A,\ldots,s_j^A,\ldots,s_N^A,s_1^B,\ldots,s_N^B \to s_1^A,\ldots,-s_j^A,\ldots,s_N^A,s_1^B,\ldots,s_N^B)$ the transition rate of the jth spin from state s_j^A to $-s_j^A$ for any value of s_j^B. The dynamics of the model are completely fixed by knowledge of the function W which is assumed independent of the previous history of the system (Markovian process).

The time evolution of this probability function is given by the following general master equation

$$\frac{d}{dt} p(s_1^A,\ldots,s_N^A,s_1^B,\ldots,s_N^B;t)$$

$$= -\sum_{j=1}^N W_j(s_j^A,s_j^B \to -s_j^A,s_j^B) p(s_1^A,\ldots,s_j^A,\ldots,s_1^B,\ldots,s_j^B;t) - \sum_{j=1}^N W_j(s_j^A,s_j^B \to s_j^A,-s_j^B) p(s_1^A,\ldots,s_j^A,\ldots,s_1^B,\ldots,s_j^B;t)$$

$$- \sum_{j=1}^N W_j(s_j^A,s_j^B \to -s_j^A,-s_j^B) p(s_1^A,\ldots,s_j^A,\ldots,s_1^B,\ldots,s_j^B;t) + \sum_{j=1}^N W_j(-s_j^A,s_j^B \to s_j^A,s_j^B) p(s_1^A,\ldots,-s_j^A,\ldots,s_1^B,\ldots,s_j^B;t)$$

$$+ \sum_{j=1}^N W_j(s_j^A,-s_j^B \to s_j^A,s_j^B) p(s_1^A,\ldots,s_j^A,\ldots,s_1^B,\ldots,-s_j^B;t) + \sum_{j=1}^N W_j(-s_j^A,-s_j^B \to -s_j^A,s_j^B)$$

$$\times p(s_1^A,\ldots,-s_j^A,\ldots,s_1^B,\ldots,-s_j^B;t). \tag{8}$$

Taking into account only one spin transitions, the previous master equation leads to detailed balance equations,

$$\frac{W_j(s_j^A,s_j^B \to -s_j^A,s_j^B)}{W_j(-s_j^A,s_j^B \to s_j^A,s_j^B)} = \frac{p_e(-s_j^A,s_j^B)}{p_e(s_j^A,s_j^B)};$$

$$\frac{W_j(s_j^A,s_j^B \to s_j^A,-s_j^B)}{W_j(s_j^A,-s_j^B \to s_j^A,s_j^B)} = \frac{p_e(s_j^A,-s_j^B)}{p_e(s_j^A,s_j^B)}, \tag{9}$$

where $p_e(s_j^A,s_j^B) = \exp[-\beta H(s_j^A,s_j^B)]$ are canonical Boltzmann probabilities. Inserting these probabilities in the last detailed balance, we arrive at.

$$\frac{p_e(-s_j^A,s_j^B)}{p_e(s_j^A,s_j^B)} = \frac{\exp[-\beta s_j^A(\varepsilon_j^A + E_j^A)]}{\exp[\beta s_j^A(\varepsilon_j^A + E_j^A)]};$$

$$\frac{p_e(-s_j^A,s_j^B)}{p_e(s_j^A,s_j^B)} = \frac{\exp[-\beta s_j^B(\varepsilon_j^B + E_j^B)]}{\exp[\beta s_j^B(\varepsilon_j^B + E_j^B)]}, \tag{10}$$

with $E_j^A = J_1 \sum_i s_i^A - (\Delta - kT \ln g)$ and $\varepsilon_j^A = J_2 \sum_i s_i^B$. E_j^B and ε_j^B can be expressed from expressions of E_j^A and ε_j^A by interchanging exponents A and B.

It is well known that several dynamic choices are possible according to Eqs. (9) and (10) which only provide the

ratio of the probabilities of opposite transition rates. Taking into account the specificity of the spin-crossover problem, in which the dynamics are of Arrhenius type at relatively high temperature, simple transformation allows us to obtain a possible choice for the transition rate that obeys the previous constraints:

$$W_B(s_j^B \to -s_j^B)$$

$$= \mathrm{tr}_{\{s_j^A\}} W_j(s_j^A,s_j^B \to s_j^A,-s_j^B)$$

$$= \frac{1}{2\tau}[\cosh\beta(\varepsilon^B + E^B) - s^B \sinh\beta(\varepsilon^B + E^B)], \tag{11}$$

$$W_A(s_j^A \to -s_j^A)$$

$$= \mathrm{tr}_{\{s_j^{BA}\}} W_j(s_j^A,s_j^B \to -s_j^A,s_j^B)$$

$$= \frac{1}{2\tau}[\cosh\beta(\varepsilon^A + E^A) - s^A \sinh\beta(\varepsilon^A + E^A)]. \tag{12}$$

The symbol $\mathrm{tr}_{\{s_j^A\}}$ represents the partial trace on the spin states s_j^A. The factor $1/2\tau = (1/2\tau_0) \exp(-E_a^0/kT)$ defines the individual spin flip rate between HS and LS states and fixes
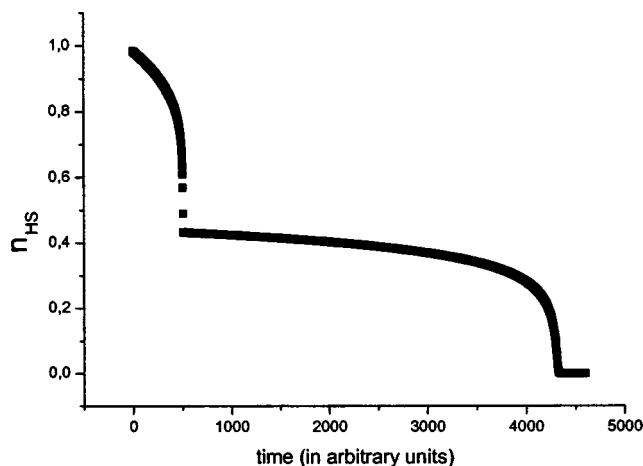
FIG. 1. Simulated relaxation curve of the high-spin fraction obtained from numerical solution of the coupled differential equations [Eqs. (16) and (17)]. The parameters used are $J_1 = 220$ K, $J_2 = -70$ K, $\Delta = 900$ K, $g = 400$, $E_0^A = 1150$ K, $\tau_0 = 0.001$ and $T = 44$ K.

FIG. 2. Experimental relaxation curve for $\{Fe(pmd)\,[Ag(CN)_2]\times[Ag_2(CN)_3]\}$ at $T = 44$ K. The inset shows the double step thermodynamical equilibrium behavior.

the time scale of the thermally activated phenomenon over the intramolecular energy barrier E_a^0 of the SC molecule. Generally the Arrhenius prefactor $1/\tau_0$ results from the intrinsic phonon frequency of the system. However in our case, $1/\tau_0$ must be seen as a temperature dependent frequency prefactor that originated from a thermal tunneling (Franck–Condon) process over the vibronic intramolecular barrier. Therefore this quantity depends on the strength of the vibronic coupling and the overlapping of the vibrational functions localized around the HS and LS states.[6,7]

Next we adopt the mean-field approach to solve this dynamical problem. In that case the expressions of E_j^A and ε_j^A can be rewritten as follows:

$$E^A = zJ_1 m_A - \left(\Delta - \frac{kT}{2}\ln g\right), \quad \varepsilon^A = J_2 m_B, \quad (13)$$

m_A and m_B are the average value of the "magnetization" in each sublattice, directly related to the associated HS fraction by $n_{HS} = (1+m)/2$. Now, in order to determine the evolution equations of $m_A(t)$ and $m_B(t)$, we use the expression of one site probability $p(s_j;t)$ given in the mean-field approximation by $p(s_j^X;t) = (1 + m_X(t)s_j^X)/2$ where $X = A$, B and $m_X(t)$ is the magnetization of sublattice X at time t.

The equations of motion associated with $m_A(t)$ and $m_B(t)$ can be obtained from the master equation using the mean-field approach and assuming the lattice to be spatially invariant. After some development we arrive at the following system of nonlinear coupled differential equations

$$\frac{dm_A}{dt} = \frac{1}{\tau}\left[\sinh\beta(E^A + \varepsilon^A) - m_A\cosh\beta(E^A + \varepsilon^A)\right], \quad (14)$$

$$\frac{dm_B}{dt} = \frac{1}{\tau}\left[\sinh\beta(E^B + \varepsilon^B) - m_B\cosh\beta(E^B + \varepsilon^B)\right], \quad (15)$$

where

$$E^A + \varepsilon^A = J_1 m_A + J_2 m_B - \Delta + (1/2)kT\ln g$$

and

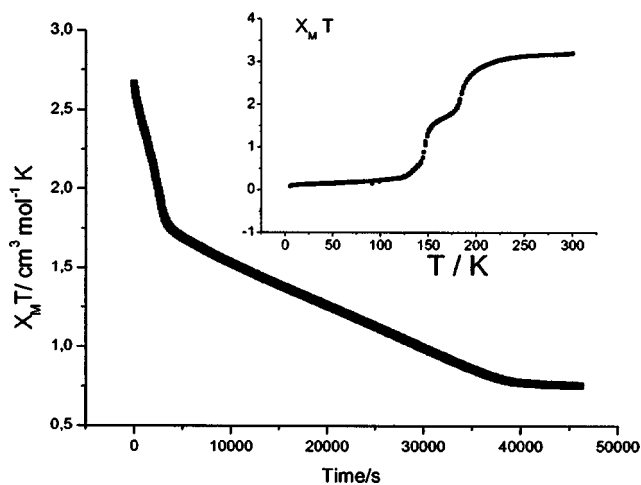$$E^B + \varepsilon^B = J_1 m_B + J_2 m_A - \Delta + (1/2)kT\ln g.$$

At thermodynamical equilibrium ($dm_A/dt = 0$ and $dm_B/dt = 0$), dynamical Eqs. (14) and (15) lead exactly to the self-consistent equations (3) obtained in the static approach of Sec. II.

IV. LOW TEMPERATURE REGIME

At low temperature, the equations of motion, Eqs. (14) and (15), become

$$\frac{dm_A}{dt} = -K_0(T)\frac{1+m_A}{2}\exp[-(\alpha_2 m_B + \alpha_1 m_A)], \quad (16)$$

$$\frac{dm_B}{dt} = -K_0(T)\frac{1+m_B}{2}\exp[-(\alpha_2 m_A + \alpha_1 m_B)], \quad (17)$$

with $\alpha_i = \beta J_i$ ($I = 1,2$) and $K_0(T) = 1/\tau\exp\beta[-E_a^0 + \Delta - (kT/2)\ln g]$; with β being $1/kT$.

It is worth noting that we find again by this simple microscopic approach exactly the same macroscopic equations of motion we have used in the past[8] to describe phenomenologically the irradiation effect in these systems.

With the intersublattice interaction J_2 being negative, it becomes possible beyond a critical value of J_2 to obtain relaxation curves with two regimes. This relaxation in two steps is shown in Fig. 1, in which we have reported the temporal evolution of the total high-spin fraction $n_{HS} = n_{HS}^A + n_{HS}^B$ as observed experimentally[3] (see Fig. 2).

[1] P. Gütlich, A. Hauser, and H. Spiering, Angew. Chem. Int. Ed. Engl. **33**, 2024 (1994).
[2] A. Bousseksou, J. Nasser, J. Linares, K. Boukheddaden, and F. Varret, J. Phys. I **2**, 1381 (1992).
[3] J. A. Real and V. Niel, TOSS-Meeting 2002, 1–3rd March (2002), Seeheim, Germany.
[4] K. Boukheddaden, I. Shteto, B. Hoo, and F. Varret, Phys. Rev. B **62**, 14796 (2000).
[5] R. J. Glauber, J. Math. Phys. **4**, 294 (1963).
[6] A. Hauser, Coord. Chem. Rev. **111**, 275 (1991).
[7] E. Bukhs, G. Navon, M. Bixon, and J. Jortner, J. Am. Chem. Soc. **102**, 2918 (1980).
[8] C. Parreira, C. Enachescu, J. Linares, K. Boukheddaden, and F. Varret, J. Phys.: Condens. Matter **12**, 9395 (2000).