Simulations of Edge Effect in 1D Spin Crossover Compounds by Atom-Phonon Coupling Model

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Open Access Journal of Physics: Conference Series (JPCS) (in press)

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Abstract. We used the atom-phonon coupling model to explain and illustrate the behavior of a linear nano-chain of molecules. The analysis of the system's behavior was performed using Free Energy method, and by applying Monte Carlo Metropolis (MCM) method which take into account the phonon contribution. In particular we tested both the MCM algorithm and the dynamic-matrix method and we expose how the thermal behavior of a 1D spin crossover system varies as a function of different factors. Furthermore we blocked the edge atoms of the chain in its high spin state to study the effect on the system's behavior.

1. Introduction

Spin crossover (SCO) is a typical example of molecular bistability, in which a diamagnetic low-spin (LS) and a paramagnetic high spin (HS) states are reversibly switchable by the application of different physical causes such as a magnetic field, pressure, light, temperature or electrical field [1-8].. Although the interest in SCO materials is essentially directed towards future multi-sensing and nano-electronics devices, the ST transition still remains one of the main goals for the physics community.

The ST transition behaviour which depends not only on external factors but also on internal factors in solid state materials, is known to be characterized by different responses such as a gradual transition, an abrupt transition, a multi step-transition with or without hysteresis or an incomplete transition under pressure. To explain the competition between the LS and HS states and moreover, to give a clear image of the spin transition phenomenon, various models such as the Ising-like model [9-12], the atom-phonon coupling model (APC) [13,14] or the mechano-elastic model [15,16], have been developed over the years.

Considering spring-like atoms characterized by three elastic constants function of the atoms' state, Nasser proposed in 2001 [13] the APC model to give a clear and wide view of the ST process in the SCO compounds. In this model three constants are defined such as: $\lambda = C_{LL}$ - the atoms are in the low spin state, $\mu = C_{LH}$ - one atom is in the low spin state and the other atom is in the high spin state, $\nu = C_{HH}$ - the atoms are in the high spin state.

2. The model

Since a detailed description of the model can be found in this paper [14], only some aspects are illustrated in this section and only some equations which are prerequisite to describe this work are recalled. To study the behaviour of SCO systems in the framework of the APC model, a circular chain of N atoms interconnected by a spring is considered. The elastic constant which have already been presented in the introduction are assumed to verify the inequalities: $\lambda > \mu > \nu$. To present the electronic state of the atoms, each electronic state of the atoms is associated to a fictitious spin operator σ which can take two eigenvalues +1 or -1 as a function of the atom state (HS or LS). The Hamiltonian is given as a sum of two terms, the spin Hamiltonian and phonon Hamiltonian:

$$H = H_{spin} + H_{phonon} \tag{1}$$

with: $$H_{spin} = \sum \frac{\Delta}{2}\sigma_i \quad \text{and} \quad H_{phonon} = \sum g^{nhs} B(f_i) \tag{2}$$

In equation 2, the spin Hamiltonian depends on Δ, the difference in energy between the two electronic levels (LS) and (HS) and the phonon Hamiltonian depends on the degeneracy g^{nhs} and the Boltzmann factor $B(f_i)$.

The Hamiltonian given by Equation 1 can be solved in two different cases as discussed in sections 2.1 and 2.2.

2.1. Dynamic Matrix method and Monte Carlo Metropolis algorithm

According to the dynamic matrix method described in [17], the partition function can be written as:

$$Z_{ph}^{i} = g^{nhs_i} e^{-\frac{\beta\Delta}{2}m_i} \prod_{i=1,N} \left[2\sinh\left(\frac{\hbar\omega_i}{2k_B T} \right) \right]^{-1} \tag{3}$$

In constructing the dynamic matrix, from all the states distribution, it is necessary to group together configurations which have the same value of the partition function (Z). Thus the parameter "nbre(nhs)" is defined to account for the sum of the configurations with the same "nhs" value and with the same eigen values (frequency).

$$Z_{ph} = \sum_{i=1,N} \left\{ nbre(nhs) Z_{ph}^{i} \right\} \tag{4}$$

Using MCM algorithm described in [18] the switching probability between the old state and the new state, P, is given by the next equation:

$$P_{state} = \frac{g^{nhs_{new}} e^{-\frac{\beta\Delta}{2}m_{new}} \prod_{i=1,N} \left[2\sinh\left(\frac{\hbar\omega_{new}}{2k_B T} \right) \right]^{-1}}{g^{nhs_{old}} e^{-\frac{\beta\Delta}{2}m_{old}} \prod_{i=1,N} \left[2\sinh\left(\frac{\hbar\omega_{old}}{2k_B T} \right) \right]^{-1}} \tag{5}$$

2.2. Free energy

In the free energy method the magnetization M is calculated as follows:

$$M = \frac{\sum m_i \deg \xi_i}{\sum \deg \xi_i} \frac{1}{N} \tag{6}$$

where *deg* is the number of configurations with the same eigen value.

The high spin fraction n_{HS} giving the ratio between the number of atoms in the high spin state and the total number of atoms is defined as:

$$n_{HS} = (1+M)/2 \tag{7}$$

Using the following formula to calculate the free energy, F, we are able to study the stability of the system's state:

$$F(n_{HS}) = -Tln\left(\sum_{i=1}^{N} \xi_i\right) \tag{8}$$

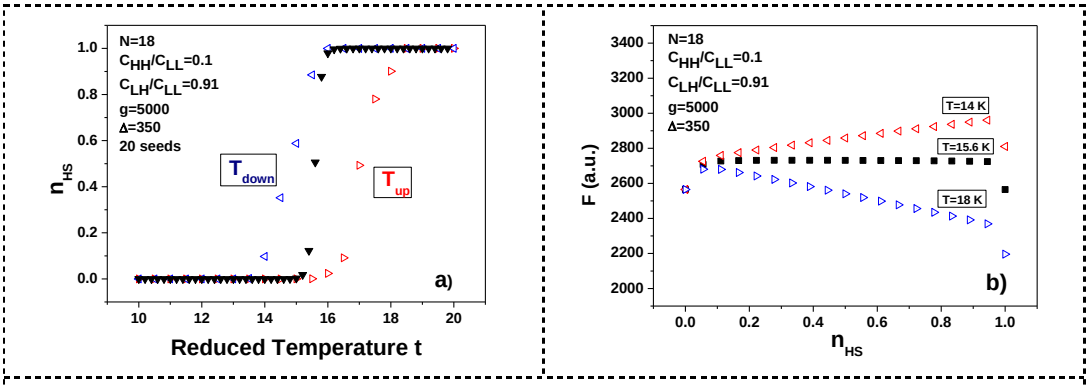

Figure 1. a) the simulated HS fraction, n_{HS}, as a function of the temperature and b) the free energy for three different temperature for an **A** type system.

Figure 1 a) and b) show the evolution of the HS fraction, n_{HS}, as a function of temperature and the free energy for three different temperatures. In figure 1 a) besides the red curve, when the temperature is increasing and the blue curve when the temperature is decreasing (obtained by transfer matrix method and Monte Carlo Metropolis algorithm), the results obtained by the numerical calculation previously described are plotted in black.

3. The role of edge atoms

To explain the role of edge atoms two types of systems were considered: an **A** type system in which the molecules are either HS and (or) LS and a **B** type system in which we add and fix at the beginning and at the end, one atom in the HS state to an **A** type system. In this case the system **A** can be **HS**……**HS-LS**……**LS** while the system **B** is of the form **HS**+**LS**……**HS-LS**……**LS**+**HS**. The evolution of HS fraction, n_{HS}, for an **A** type system is reported in figure 1 a) with the free energy in figure 1 b). In figures 2 a) and b) are reported the HS fraction and the free energy for three different temperatures for a **B** type system. The comparison of the results reported in figure 1 a) with figure 2 a) shows that by adding and fixing the edge atoms in HS state, the transition temperature is shifted to a lower temperature and the width of hysteresis loop is decreased. Moreover the transition is more abrupt.

4. Conclusions

In this work the thermal behaviour of a 1D spin crossover system under the action of edge atoms (HS), in the framework of the atom-phonon coupling model is studied, using Monte Carlo Metropolis algorithm combined with transfer matrix method and the Free energy method. By taking into account the phonons contributions, the hysteretic behaviour of a 1D system is reproduced without having to consider the long-range interactions.

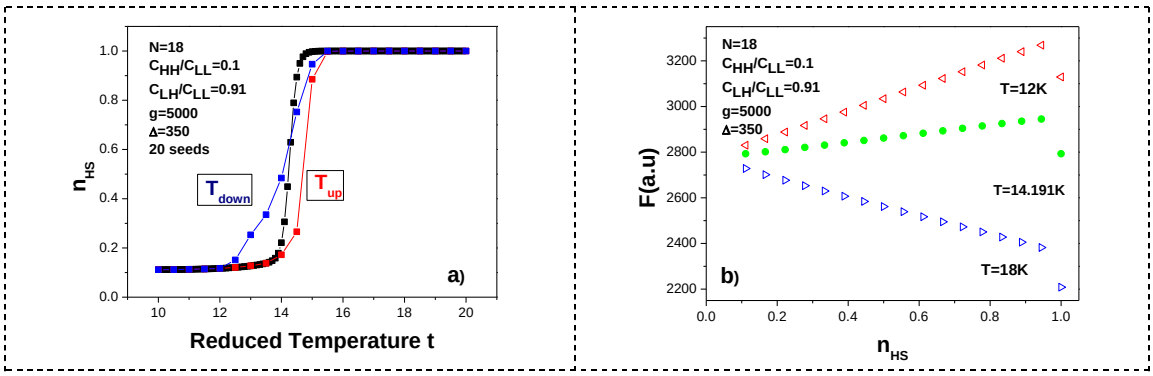

Figure 3. a) the simulated HS fraction, n_{HS}, as a function of the temperature and b) the free energy for three different temperatures for a **B** type system.

Acknowledgments

The authors would like to thank Professor J.A. Nasser for useful discussions. CHAIR Materials Simulation and Engineering, UVSQ, Université Paris Saclay is gratefully acknowledged.

References

[1] Bousseksou A, Molnar G, Salmon L and Nicolazzi W 2011 *Chemical Society Reviews* **40** 3313-35
[2] Gütlich P 2013 *European Journal of Inorganic Chemistry* 581-91
[3] Gutlich P, Ksenofontov V and Gaspar A 2005 *Coord Chem Rev* **249** 1811 - 29
[4] Rotaru A, Dugay J, Tan R P, Gural'skiy I A, Salmon L, Demont P, Carrey J, Molnar G, Respaud M and Bousseksou A 2013 *Advanced Materials* **25** 1745-9
[5] Jureschi C-M, Rusu I, Codjovi E, Linares J, Garcia Y and Rotaru A 2014 *Physica B: Condensed Matter* **449** 47-51
[6] Jureschi C M, Linares J, Rotaru A, Ritti M H, Parlier M, Dîrtu M M, Wolff M and Garcia Y 2015 *Sensors (Basel, Switzerland)* **15** 2388-98
[7] V. Mishra, R. Mukherjee, J. Linares, C. Balde, C. Desplanches, J.F. Létard, E. Collet, L. Toupet, M. Castro, F. Varret, Inorg Chemistry, *47, 7577-7587 (2008)*
[8] S. Klokishner, J. Linares, F. Varret, Chemical. Physics, **255** (2000), 317-323
[9] Wajnflasz J and Pick R 1971 *J. Phys. Colloques* **32** C1-91-C1-2
[10] Bousseksou A, Nasser J, Linares J, Boukheddaden K and Varret F 1992 *Journal De Physique I* **2** 1381-403
[11] Boukheddaden, K; Linares, J; Codjovi, E; Varret, F; Niel, V; Real, JA, Journal of Applied Physics, **93** (2003) 7103-7105
[12] I. Shteto, J. Linares, F. Varret, Physical Review E 56 (1997) 5128-5137
[13] Nasser J A 2001 *European Physical Journal B* **21** 3-10
[14] Nasser J A, Boukheddaden K and Linares J 2004 *European Physical Journal B* **39** 219-27
[15] Enachescu C, Nishino M, Miyashita S, Stoleriu L and Stancu A 2012 *Physical Review B* **86** 054114

[16] Chakraborty P, Enachescu C and Hauser A 2013 *European Journal of Inorganic Chemistry* 770-80
[17] Chiruta D, Jureschi C M, Linares J, Nasser J and Rotaru A 2015 *Physica B: Condensed Matter*
[18] Rotaru A, Carmona A, Combaud F, Linares J, Stancu A and Nasser J 2009 *Polyhedron* **28** 1684-7