



## Research paper

Surface transition in spin crossover nanoparticles<sup>☆</sup>Mirko Mikolasek<sup>a,b</sup>, William Nicolazzi<sup>a,\*</sup>, Ferial Terki<sup>b</sup>, Gábor Molnár<sup>a</sup>, Azzedine Bousseksou<sup>a</sup><sup>a</sup> Laboratoire de Chimie de Coordination, CNRS UPR-8241 and Université de Toulouse, UPS, INP, Toulouse, France<sup>b</sup> Institut Charles Gerhardt, Université Montpellier 2, place Eugène Bataillon, Montpellier, France

## ARTICLE INFO

## Article history:

Received 7 February 2017

In final form 10 April 2017

Available online 11 April 2017

## Keywords:

Spin crossover

Nanoparticles

Surface relaxation

## ABSTRACT

The spin transition in a square lattice nanoparticle, whose the primitive cell is constituted of 2 metallic centres, is investigated using a two-variable elastic Ising-like model solved by Monte Carlo simulations. We show that the specific lattice geometry can lead to an important surface relaxation of both the structure and the spin-state, which are analysed by mapping the local strain. The consequence of this surface relaxation is the occurrence of a stepwise spin transition where the surface and the core switch at different temperatures.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

The spin crossover (SCO) phenomenon is an exciting example of molecular bistability in which a transition metal ion with a  $3d^4$ - $3d^7$  electronic configuration can exhibit a reversible switching between the molecular low-spin (LS) and the high-spin (HS) states upon the application of external stimuli such as temperature or pressure variations, light irradiation or an intense magnetic field [1]. This phenomenon is accompanied by important modifications of the molecular and crystal structure. In particular, when going from the LS to the HS state, the metal-ligand distances increase [by ca. 10% ( $\sim 0.2$  Å) in the case of Fe(II)  $N_6$  octahedron], which is also associated with a decrease of the vibrational frequencies of the molecule. In the solid state, the increase of the metal-ligand distances leads to an increase of the volume of the primitive cell by several percent, up to 13% for the compound Fe(pyrazine)[Pt(CN)<sub>4</sub>] [2]. Due to the important volume variation between the two spin states, a switching molecule causes local elastic distortions, which propagate through the crystal packing. Such collective behaviours, the so-called cooperativity, can induce a first-order phase transition with the presence of a hysteresis loop [3,4].

These last years, with the appearance of new SCO nano-objects, such as thin films, nanoparticles and nanopatterns [5–7], size reduction effects have received a growing interest. The experimental observations revealed a variety of finite-size effects in different SCO compounds, which can be related to the large structural

diversity of these materials (mono-, bi- and polynuclear complexes) and also to the numerous physico-chemical phenomena which are involved (eg. surface, confinement and kinetic effects). Nevertheless, the decrease of the cooperativity, the downshift of the transition temperature and the occurrence of incomplete transitions seem to be the general trend at reduced sizes. Simple thermodynamical considerations indicate all these observations can be explained by a higher surface energy in the LS state, which tends to stabilize the HS state on the surfaces [8]. Obviously, the fact that the metal complexes on the surface are blocked in the HS state has a dramatic consequence on the SCO properties of small nanoparticles [9]. From a theoretical point of view, this can be modelled either by *ad-hoc* freezing the spin-state of surface molecules [10–13] or by assuming an additional surface energy term in the Hamiltonian of the system [14].

Another interesting ingredient, which has not yet been investigated is surface relaxation. In this paper, we show that due to the strong electron-phonon coupling, a surface spin-state relaxation can occur for specific lattice geometries, leading to a stabilization of the HS state on the surface. Interestingly, the surface molecules display also a spin transition, but at much lower temperature than the molecules in the particle core.

## 2. Model and method

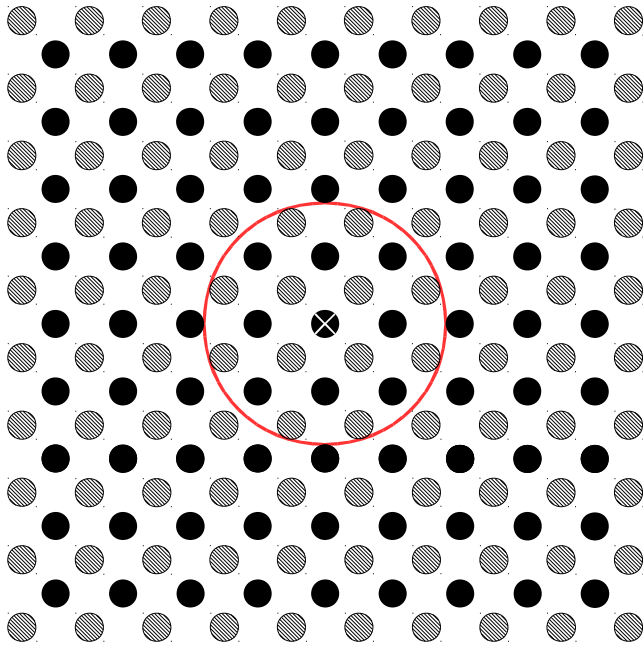
## 2.1. Hamiltonian

In the following, we describe the spin-phonon model introduced in previous works [15]. Let's consider a primitive square cell made of 2 metallic centres, represented in Fig. 1, constituted of  $N_M = 9^2$  inactive centres and  $N_{SCO} = 10^2$  active metallic centres.

<sup>☆</sup> Fully documented templates are available in the elsarticle package on CTAN.

\* Corresponding author.

E-mail addresses: [william.nicolazzi@lcc-toulouse.fr](mailto:william.nicolazzi@lcc-toulouse.fr) (W. Nicolazzi), [azzedine.bousseksou@lcc-toulouse.fr](mailto:azzedine.bousseksou@lcc-toulouse.fr) (A. Bousseksou).



**Fig. 1.** Schematic representation of the simulated particle. Black filled circles (hatched circles) represent the inactive (active) metallic centres. The red circle indicates the interaction range of Lennard-Jones potentials acting on the central metal ion, marked by a white cross. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The vibronic states of these latter are described by the following two-level Hamiltonian:

$$\mathcal{H}_{\text{intra}} = \frac{1}{2}(\Delta - k_B T \ln(g_{\text{HS}}/g_{\text{BS}})) \sum_{i=1}^N \sigma_i \quad (1)$$

where  $T$  is the temperature and  $k_B$  the Boltzmann constant.  $\sigma_i = \pm 1$  (+1 for the HS state and  $-1$  for the LS state) are the eigenvalues of the fictitious spin operator, which represent the spin state of the  $i^{\text{th}}$  active metallic centre.  $\Delta$  represents the energy difference at  $T = 0$  between the two vibronic states. This term stabilizes the LS state while the vibrational and the electronic degeneracy ratio of the two states,  $g_{\text{HS}}/g_{\text{BS}}$ , tends to stabilise the HS state at high temperatures.

In order to take into account the lattice degrees of freedom, anharmonic potentials are considered between the metallic centres such as:

$$\mathcal{H}_{\text{inter}} = \sum_{\langle ij \rangle} V_{\text{el}}(\sigma_i, \sigma_j, r_{ij}) + \sum_{\langle\langle ij \rangle\rangle} V_{\text{el}}(\sigma_i, \sigma_j, r_{ij}) + \sum_{\langle\langle\langle ij \rangle\rangle\rangle} V_{\text{el}}(\sigma_i, \sigma_j, r_{ij}) + \sum_{\langle\langle\langle\langle ij \rangle\rangle\rangle} V_{\text{el}}(\sigma_i, \sigma_j, r_{ij}) \quad (2)$$

where  $\sum_{\langle ij \rangle}$ ,  $\sum_{\langle\langle ij \rangle\rangle}$ ,  $\sum_{\langle\langle\langle ij \rangle\rangle\rangle}$  and  $\sum_{\langle\langle\langle\langle ij \rangle\rangle\rangle}$  are the sum over the first, second, third and fourth neighbours respectively and  $V_{\text{el}}(\sigma_i, \sigma_j, r_{ij})$  is a 12-6 Lennard-Jones potential defined as:

$$V_{\text{el}}(\sigma_i, \sigma_j, r_{ij}) = A_{\text{XY}} \left[ \left( \frac{r_{\text{XY}}}{r_{ij}} \right)^{12} - 2 \left( \frac{r_{\text{XY}}}{r_{ij}} \right)^6 \right] \quad (3)$$

$X$  and  $Y$  represent the type of metallic centre and its spin state (H and L for an active metallic centre in the HS and LS states respectively and M for an inactive metallic centre).  $r_{\text{XY}}$  is the spin state equilibrium distance and  $r_{ij}$  is the spontaneous distance between the metallic centres  $i$  and  $j$ .  $A_{\text{XY}}$  is the spin state dependent bond energy at  $T = 0$  K.

Two types of interactions are taken into account. (i) Interactions between active and inactive metallic centres (first and third neighbours). In this case the electron-phonon coupling is taken into account by considering spin state dependent parameters with equilibrium distances of  $r_{\text{LM}} = 5.0 \text{ \AA}$  in the LS state and of  $r_{\text{HM}} = 5.2 \text{ \AA}$  in the HS state. (ii) Interactions between two active or two inactive metallic centres. In this case, we make the assumption the inactive metallic centres stabilize the LS state and all the equilibrium distances of second and fourth neighbours are defined as  $r_{\text{HH}} = r_{\text{LL}} = r_{\text{HL}} = r_{\text{MM}} = 5.0\sqrt{2} \text{ \AA}$ . To decrease the number of parameters, bond energies  $A$  are defined as  $A_{\text{HH}} = A_{\text{LL}} = A_{\text{MM}} = 7200 k_B \cdot K$  except the spin state interface energy which is defined as  $A_{\text{HL}} = 7100 k_B \cdot K$ . The more important stiffness of the LS state is taken into account through the change of the concavity of the potential due to the smaller equilibrium distance. Table 1 summarises the considered parameters.

The total Hamiltonian can be written as:

$$\mathcal{H}_{\text{tot}} = \mathcal{H}_{\text{intra}} + \mathcal{H}_{\text{inter}} \quad (4)$$

This simple system allows to investigate the role of the structure in the spin transition at the nanoscale. It bears resemblance to the 2D coordination networks of the general formula  $[\text{Fe}(\text{pyridine})\text{M}(\text{CN})_4]$  with  $\text{M} = \text{Ni}, \text{Pt}, \text{Pd}$  [16,17], but it can be also considered as a solid solution where active metal ions (eg. Fe) are replaced by inactive metal ions (eg. Zn) [18,19]. In the latter case, the inactive centres are supposed to have the same ionic radius as the active centres in the LS state.

## 2.2. Methods

In order to investigate the SCO properties, the thermodynamical quantities are estimated by Monte Carlo methods in the isothermal and isobaric ensemble ( $T, P = 0, N$ ) using the Metropolis algorithm [20]. To follow the spin transition, we define the high spin fraction  $n_{\text{HS}}$  which represents the mean number of active centres in the HS state:

$$n_{\text{HS}} = \frac{1 + \langle \sigma \rangle}{2} \quad (5)$$

**Table 1**

Parameters of the modelled system. Energies have been normalized by  $k_B$ .

Equilibrium distance		Bond energy	
<i>Lattice interaction parameters</i>			
$r_{\text{HM}}$	=	5.2 $\text{\AA}$	$A_{\text{HM}}$ = 7200 K
$r_{\text{LM}}$	=	5.0 $\text{\AA}$	$A_{\text{LM}}$ = 7200 K
$r_{\text{MM}}$	=	$5.0\sqrt{2} \text{ \AA}$	$A_{\text{MM}}$ = 7200 K
$r_{\text{HH}}$	=	$5.0\sqrt{2} \text{ \AA}$	$A_{\text{HH}}$ = 7200 K
$r_{\text{LL}}$	=	$5.0\sqrt{2} \text{ \AA}$	$A_{\text{LL}}$ = 7200 K
$r_{\text{HL}}$	=	$5.0\sqrt{2} \text{ \AA}$	$A_{\text{HL}}$ = 7100 K
<i>Vibronic parameters</i>			
$\Delta$	=	1000 K	$\ln(g_{\text{HS}}/g_{\text{LS}})$ = 7.6962

Download English Version:

<https://daneshyari.com/en/article/5377950>

Download Persian Version:

<https://daneshyari.com/article/5377950>

[Daneshyari.com](https://daneshyari.com)