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Reprint of “Surface-environment effects in spin crossover solids”☆

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ABSTRACT

The impact of surface effects on thermal induced spin crossover phenomenon is a subject of a broad and current interest. Using the modified Ising-like model of spin crossover solids with the ligand field as function of the molecule’ positions and random component on surface by means of Metropolis Monte Carlo algorithm the thermal spin transition curves were calculated. The analysis of spin configuration during transition gives a general idea about contribution of molecules from the surface and inside the lattice into resulting magnetization of the systems. The behavior of hysteresis loop for various surface coupling and fluctuations strength has been described.

1. Introduction

Spin crossover (SCO) systems are relatively rare class of transition metal complexes that display molecular magnetic bistability and interconverted reversibility upon external stimuli. Under normal conditions, these complexes can exhibit spin crossover, that is, the entropy-driven thermal transition from a low-spin (LS) state, populated at low temperatures, to a high-spin (HS) state, populated at higher temperatures. The observed spin state depends on the balance between maximizing the number of parallel spins/unpaired electrons (Hunds rule) versus having the lowest electronic energy by populating the lowest energy orbitals. For a free atom or ion, or ionic compound the normal spin state is that of maximum multiplicity, in accordance to Hund’s rule, however, for sufficiently large ligand field, one obtains a low-spin ground state. Moreover a great variety of spin transition curves are found in the solid state: sharp transitions often accompanied by hysteresis, more or less gradual transitions, and sometimes incomplete transitions with residual dia- or paramagnetism. The cooperative behavior of the spin transition in the solid state demands an interaction between the HS and LS complex molecules. The largest class of SCO complexes are the Fe(II) SCO complexes. In octahedral symmetry O_h the ferrous iron molecular complexes can be converted between diamagnetic LS ($e_g^0 t_{2g}^6$) and paramagnetic HS ($e_g^2 t_{2g}^4$) states, which leads to a significant change in the metal-ligand bond length. SCO materials are known to have potential applications such as reversible high density memories, ultrafast switches (at the nanoscale), sensors of temperature and pressure, fundamental elements in display technologies, etc. Consequently SCO systems have been studied extensively both theoretically and experimentally [1–3].

If solids shrink to the nanoscale, the surface-to-volume ratio increases and the surface-environment interaction becomes a major factor for affecting material behavior. The control over functionalities at the nanoscale (in nanoparticles, nanopatterns, thin films and ultimately, single molecules) appears as a cornerstone in the elaboration of advanced materials for many very important above technologies. The individual nanoparticles possessing an abrupt transition with a thermal hysteresis loop are appealing because they can be used for information storage at the nanometric level. The variation of electronic properties and surface roughness are called “surface effects”. Such effects are ambiguous because they may have either disadvantageous or beneficial, depending on environmental conditions and material application. These properties are very sensitive to changes in external environment. The surface exhibits some disorganized fluctuations which usually are ascribed to environmental randomness. However the rational control of the behavior of these materials on a nanometric scale is highly required, especially when they are integrated into functional devices. The investigation of surface-environment effects can be realized by modern experiments with a comprehensive suite of surface-sensitive spectroscopy and microscopy tools [4]. One of the major challenges of modern technology is to stabilize the nanoparticles and the surface in order to minimize its interaction with the environment. It is obvious that surface-environment distribution

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can be neglected in the thermodynamic limit but on the other hand a molecule must always be viewed as part of its environment [5].

The current study addresses to the role of surface-environment effects of spin crossover nanocrystals in the occurrence of phase transition in the material. The important issue is to understand the interplay of cooperativity of the system and the fluctuations of its environment. It is almost obvious that molecules on surfaces have different SCO properties than the inner molecules. This may influence the properties of the whole particle in this very low size range [6]. The transition metal ions can be seriously altered at the surface of the particle. It is very likely, particularly in the case of small particles with high specific surface areas, that these Fe(II) ions “feel” considerable differences in bond strength or even suffer from coordinative defects and consequently do not exhibit SCO [7]. We are interested in phenomena that are associated with the emergence of disorganized random fluctuations in the state of the system under influence of surrounding environment.

This work is organized as follows: In Section 2, we outline the Hamiltonian and its application to the Ising-like model of spin crossover nanocrystal interacting with the surroundings; in Section 3, we discuss the results; and finally, in Section 4, we present our conclusions.

2. Ising-like model of spin crossover nanocrystal interacting with the surroundings

Since the sizes of solid nanocrystals decrease, the increase in surface area to volume ratio makes the surface-environment effects become more pronounced. Phenomenologically, the interactions in molecular spin crossover nanoparticles can be modelled in a simplest way by the Ising-like Hamiltonian

$$\mathcal{H} = -h_0\sum_i s_i - \sum_i^s h_i(t)s_i - \sum_{\langle ij\rangle}^b J_{ij}^b s_i s_j - \sum_{\langle ij\rangle}^s J_{ij}^s s_i s_j - \sum_{\langle ij\rangle}^{b-s} J_{ij}^{b-s} s_i s_j. \quad (1)$$

Here s_i is a fictitious spin (pseudospin) operator which has two eigenvalues ±1, corresponding to the HS and LS states of respective i-s molecule, $\langle ij\rangle$ denotes the summation over all nearest-neighboring spin pairs. The Ising-like Hamiltonian describes the elastic interaction between spin states via the near neighbor coupling of two-level units. The intersites short-range coupling constants J_{ij}^{α}, measured in energy units, are parameters of the theory, where $\alpha = b, s, b-s$ correspond to occupied pairs of bulk sites, surface sites and bulk-surface sites. The schematic illustration of the model composed of a bulk sites which are surrounded by a surface of one site thick is shown in Fig. 1. The number of bonds of the sites on the surface is different from the one of the sites inside the lattice. In Fig. 1 are displayed only two kind of bonds: the one for surface sites and another one for bulk sites since the interaction between the surface sites and bulk sites is considered the same as for the sites inside the lattice, i.e. the $b-s=b$ which leads to the decomposition of the Hamiltonian into bulk and surface parts.

The effective external field describing the result of surrounding action on single molecular magnet is

$$h_0 = -\frac{1}{2}(\Delta - k_B T \ln g), \quad (2)$$

where Δ stands for the energy difference between HS and LS states (the enthalpy change associated with the $LS \rightarrow HS$ conversion) for an individual spin crossover molecule, $g = g_{HS}/g_{LS}$ is the degeneracy ratio between HS and LS energy levels, k_B is the Boltzmanns constant. It is considered that the value Δ is fully formed by the ligand environment of the transition metal ion, this is why it is called the ligand field. In this version the external field is homogeneous but it depends on temperature. Thus in noninteracting system, the equilibrium temperature T_{eq}^0 at which mole fractions of the LS and HS states are equally, corresponds to a zero effective field and, consequently $T_{eq}^0 = \Delta/(k_B T \ln g)$. It is important to note for our study that T_{eq}^0 coincides with the transition temperature in the bulk material. The Hamiltonian (1) describes in a convenient way the behavior of spin crossover system where the control parameter is a temperature T. If the critical temperature in purely Ising model is smaller than the equilibrium temperature in noninteracting model, then a gradual spin transition from LS to HS takes place by increasing the temperature. Otherwise, the spin transition is discontinuous and is associated to a first-order phase transition. In turn, $h_i(t)$ is seen to correspond to the randomly fluctuating ligand field. The $h_i(t)$ is the random field only at site i on the ideal (sharp) surface of the bulk material. Indeed, the ligand field as function of the molecules' positions in the lattice is the key point of examination of surface effects leading to unusual size dependence of the thermal hysteresis behavior in spin crossover nanoparticles [8]. Linares et al [8] included the interaction between the edge molecules and the environment as a negative (but non uniform) pressure on the system through the interaction of surface atoms with their nearest neighboring atoms situated inside the lattice. The local pressure acting on the edge spin crossover molecules from the matrix side during transition from HS to LS states was considered in paper [9]. This idea arises from the mechanoelastic model where local pressure changes at the edge molecules are taken into account by missing springs [10]. The same idea was used by Tissot et al. [11] to explain the experiments of control of the thermal hysteresis of the prototypal spin-transition in $Fe^{II}(phen)_2(NCS)_2$ compound via the microcrystallites environment. Muraoka et al. [12] considered the edge molecules as inactive HS ones whereas all inside molecules are active in the framework of the Ising-like model. We proceed somewhat differently. Since a Gaussian stochastic process is archetypical for contact with thermal surrounding system we use the statistical characteristic of the fluctuating external field as follows

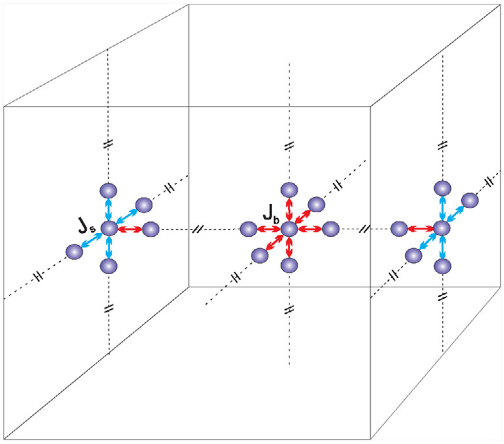

Fig. 1. The spatial configuration of a three-dimensional SCO system where is showing the difference between the interactions of magnetic molecules situated on the surface and inside the lattice.

$$\langle h_i(t)\rangle = 0, \ \langle h_i(t)h_j(t')\rangle = \varepsilon^2 \delta_{ij}\delta(t-t'). \quad (3)$$

Here $\langle \ldots \rangle$ represents an ensemble average over all realizations of the fluctuating field. Besides ε is a measure of the strength of random surface fields, δ_{ij} is the Kronecker delta symbol. The basic idea behind Langevin approach is to assume that the fluctuations on each atomic site can be represented by a Gaussian white noise term. Stronger fluctuations lead to increasing the width of the Gaussian distribution.

In the usual consideration, each molecule on surface is assumed to be instantaneous coupled to a thermal reservoir and heat currents may arise between the reservoirs in the stationary state

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