Polyhedron 66 (2013) 108–115

Contents lists available at SciVerse ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Artificial Neural Network modeling of spin-transition behavior in two-dimensional molecular magnet: The learning by experiences analysis

Wimalin Laosiritaworn [a,*], Yongyut Laosiritaworn [b,c]

[a] Department of Industrial Engineering, Faculty of Engineering, Chiang Mai University, Chiang Mai 50200, Thailand
[b] Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
[c] Thailand Center of Excellence in Physics, Commission on Higher Education, Ministry of Education, Bangkok 10400, Thailand

ARTICLE INFO

Article history:
Received 7 January 2013
Accepted 28 February 2013
Available online 7 March 2013

Keywords:
Artificial Neural Network
Ising model
Molecular magnet
Monte Carlo
Spin-transition
Thermal hysteresis

ABSTRACT

In this work, the spin-transition behavior in molecular magnet was investigated via Monte Carlo simulation on Ising model with mechano-elastic interaction extension. The initial spin-arrangement took hexagonal lattice structure in two dimensions, where spin molecules situated on the hexagonal lattice points were allowed to move under spring-type elastic interaction potential. Metropolis algorithm was used to update the spin configurations and thermal hysteresis loops were recorded to extract the hysteresis properties, such as period-average magnetization, loop area, loop width and height, as functions of parameters associated to magnetic and elastic interaction in the Hamiltonian. From the Monte Carlo results, the dependence of the hysteresis loop characteristic on magnitude of energy differences and number of available states between the low spin state and the high spin state was evident. The occurrence of the cooperative effect was notable, in agreement with previous experimental investigation, when the range of Hamiltonian parameters used is appropriate. Then all the measured hysteresis characteristic were passed to the Artificial Neural Network modeling to create extensive database of how the thermal hysteresis would respond to the change of molecular magnet Hamiltonian parameters. The scattering plots between the Artificial Neural Network and the real measured results have *R*-square closed to one which confirms the success of Artificial Neural Network in modeling this thermal hysteresis behavior. One is therefore allowed to use this Artificial Neural Network database as a guideline to design ultra-thin-film molecular magnet application in the future.

1. Introduction

To continuously serve the customers' great need in information industries, there has been an intense interest on enhancing storage capacity. This therefore inspires the pursuit for materials that can present stable bi-molecular states. One persuasive candidate is the spin-transition material: a molecular magnet with bi-switchable states between low spin state (LS) and high spin state (HS) [1]. Due to more occupied orbitals, the HS volume is larger than that of the LS [2–3]. Differences between these volumes during spin-transition induce material distortions leading to spring-like interactions. Transition between states can be enhanced by heat, magnetic field, light or stresses, which changes materials magnetic properties [4–7]. For instance, with increasing environmental temperatures, there occurs thermal spin-transition in molecular magnets (the so called thermal spin-crossover) from the low spin state (LS) at low temperatures to the high spin state (HS) at high temperatures. Further, depending on the magnitude of intermolecular interactions, the thermal spin-transition from low-to-high and high-to-low temperatures can be of the same or different characteristics (in forming thermal hysteresis phenomena or the cooperative effect), which makes spin-transition compound become a promising candidate for future high-density information storage media [8–10]. Although number of theoretical studies has been performed in supporting experiments to accelerate both technological and fundamental developments, there are still incomplete pictures in the fundamental understanding. Specifically, to establish general accessible model, relevant Hamiltonian parameters are usually defined dimensionless and varied to investigate the transition behavior. However, there are considerable numbers of relevant parameters in the Hamiltonian, so the investigation with extensive range of the parameters is somewhat limited. Some studies had to choose a specific set of well-defined parameters to model the problem [11–20]. Although with some fascinating success, those studies were limited to the specified parameters and the results are based on case by case basis. Moreover, it is known that different magnitudes of interactions between spin states results in various types of the thermal hysteresis behavior such as the cooperative phenomena between the LS and HS phases; hence, some physics may be left out due to the limitation in the magnetic

* Corresponding author. Tel.: +66 53944126ex313; fax: +66 53944185.
E-mail addresses: wimalin.l@cmu.ac.th, wimalin@hotmail.com (W. Laosiritaworn).

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http://dx.doi.org/10.1016/j.poly.2013.02.071

and mechano-elastic interaction ranges. Consequently, this study investigates the thermal hysteresis properties in a model capable of presenting molecular magnet that has bi-stable states (with size differences between these bi-stable states), and the magnetic spins have ability to move in space under an elastic interaction. Further, to overcome the limitation in the allowed ranges of the parameters problem, Monte Carlo (MC) simulation [21–22] was used alongside with the Artificial Neural Network (ANN) modeling [23–24] in extracting the thermal hysteresis behavior over extensive ranges of parameters.

To briefly outline, the ANN modeling is mathematical technique having an ability to 'learn' from experiences in establishing complex relationships among parameters, while the MC is a stochastic technique using the system inherited probability to reveal system behavior. Then, this work began with proposing the Ising Hamiltonian with mechano-elastic interaction in representing spin-transition molecules and magnetic interaction among them [11–20]. All spin-transition molecules, represented by Ising spins, were initially at the HS states arranging themselves on two-dimensional hexagonal structure. Then with varying input parameters which are the molecular radius ratio of the HS radius to the LS radius, the energy differences between the HS and LS, the degeneracy ratio between the HS and the LS, the temperature changing rate T_{freq}, and the maximum temperature away from its critical point T_{amp}, MC simulation was used to extract the average magnetization per spin and recorded as a function of temperature in constructing steady-state thermal-hysteresis. Then, the ANN modeling was performed to relate how the hysteresis properties depend on input parameters with multilayer perceptron infrastructure [23–24], i.e., one input layer (containing input parameters), two hidden layers, and one output layer (containing the thermal hysteresis properties). This was done by training the ANN with varying number of neurons in hidden layer to find the network with the best accuracy, and optimized network was used to predict the outputs from untrained sets of inputs, in drawing dynamic thermal hysteresis phase diagram. Details of these MC and ANN procedures are given in the next sections, with prominent findings presented in the results and discussion section and summarized in the conclusion section.

2. Monte Carlo simulation

The Monte Carlo (MC) technique/simulation is a stochastic method which helps to generate/predict results based on some known probabilities. Hence, the MC is really useful when the system ensemble is very large where all analytic approaches fail, even numerically, to achieve results within an allowed time frame [25]. As a result, the MC has been proved to be useful in many fields ranging from physical science, health science, finance, computer game industries, etc. In materials science or condensed matter physics areas, typical thermal MC simulation starts with proposing Hamiltonian of the studied physical system (e.g., consider Ref. [26] and references therein). Then, by minimizing the system energy, the system arrives in thermal equilibrium or steady state configurations. After that, due to thermal fluctuation, the time dependent configurations have to be quantitatively sampled to yield the representative of the system observables. Therefore, to investigate the thermal hysteresis behavior, e.g., the hysteresis shape and width (or cooperative characteristic which tells how the spin-transition depends on cooling and heating history), this work considered the Ising Hamiltonian using the short-ranged Wajnflasz–Pick version [27] with long-ranged elastic interaction addition as [11,18].

$$H = -J\sum_{\langle ij\rangle} s_i s_j + \frac{1}{2}\sum_i (D - kT\log g)s_i + \frac{1}{2}k_{el}\sum_{\langle ij\rangle}(|\vec{r}_i - \vec{r}_j| - (R_i + R_j))^2. \quad (1)$$

In Eq. (1), the spin s_i equals to +1 for the HS and −1 for the LS, $\langle ij\rangle$ indicates that the sum includes only nearest neighboring pairs, J is the spin short-range exchange interaction, D is the energy difference between the low spin state (LS) and high spin state (HS), $\log g$ is the natural logarithmic function of the degeneracy ratio between the HS and the LS where $-kT\log g$ suggests how strong is the chemical potential driving force in the system [28], and k_{el} is the effective elastic interaction among the spins (the spin-transition molecules). Further, $\vec{r}$ is a vector referring to a spin position (location) away from a fixed origin, and $R_i = R_i(s_i)$ is the spin molecular magnet radius which depends on the spin state s_i i.e., $R_i = R_{HS}$ for HS ($s_i = +1$) or $R_i = R_{LS}$ for LS ($s_i = -1$). In this work, both distance and spins were set dimensionless, $J = 1$ was set as energy unit, and k_{el} was fixed at 1 J. Therefore, with this energy setting, temperature in this work has a unit of J/k, where k is the Boltzmann's constant.

In general, the competition between D and $\log g$ determines which state (LS or HS) is the preferred state. For instance, if D is much larger than $\log g$, the systems will stay at LS even at high temperatures. On the other hand, if $\log g$ is much larger than D, the systems will stay at HS even at low temperatures. Nevertheless, at some intermediate proportion of D and $\log g$ (and kT), and with long-ranged elastic interaction, thermal hysteresis with cooperative characteristic (the presence of hysteresis width at temperatures where number of LS equals to that of the HS) becomes evident. For instance, Fig. 1 shows thermal hysteresis examples from MC simulation using $D = 15$ and $\log g = \{2,4,6\}$ which confirm such behavior. As is seen, for low $\log g$ (e.g., $\log g = 2$), the magnetization stays close to its minimum ($m = -1$) which infers that the LS is of preference, so the period-average magnetization $Q = \frac{1}{\text{thermal field period}}\oint m\,dt'$ is negative. On the other hand, with increasing $\log g$ to some intermediate value (e.g., $\log g = 4$) the hysteresis width as well as the cooperative characteristic become evident while the loop starts to gain some symmetry, so Q approaches zero. At the high $\log g$ (e.g., $\log g = 6$), there are large number of available HS so the chemical potential of the HS is satisfactorily low (if temperature is not too small) so the HS is favored and magnetization stays closes to its maximum ($m = 1$). In this case, the loop symmetry is rather poor and Q becomes positive.

Although the competition between D and $\log g$ yields various striking thermal hysteresis phenomena; many previous studies fixed/chose few sets of $\{D, \log g\}$ in their investigation of hysteresis phenomena to make the calculation computationally feasible. This therefore leaves a large window of opportunities in clarifying how extensive the range of $\{D, \log g\}$ should be in giving appropriate and desired thermal hysteresis behavior. Therefore, in this work, how D and $\log g$ play their roles in determining thermal hysteresis will be another step clarified using MC simulations. However, due to many degrees of freedom making simulations over the extensive ranges of Hamiltonian parameters become computationally impractical, an artificial intelligence technique namely ANN is compulsory in filling the gap.

In this work, the MC procedure was performed on the two-dimensional hexagonal lattice (i.e., the triangular lattice), as only single k_{el} is needed for this thermal hysteresis investigation [13] and many molecular magnet materials do exist in hexagonal form (e.g., Refs. [29–31]). The considered lattice consisted of $N = L^2$ spins where L is the system linear dimension that was set to $L = 20$. Results from larger L's are not much qualitatively different. Steps of how to perform MC simulation can be displayed as the flowchart in Fig. 2. The input parameters to the simulation were the spherical radius ratio of the HS radius to the LS radius ($r = R_{HS}/R_{LS}$), D, $\log g$, the temperature sweeping rate T_{freq} and the maximum temperature away from the critical point T_{amp}, where their ranges used in this work can be found in Table 1 (rows labeled by input and column labeled by actual range). The critical temperature (T_C) of the