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Magnetic Phase Transitions in Electro-Elastic Model for Magnetically-Ordered Spin-Crossover Solids

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Abstract

Spin-Crossover (SCO) and Prussian Blue Analogs (PBAs) materials are investigated in two-dimension with the three-state Blume-Emery-Griffiths (BEG) model where each spin interacts with its nearest-neighbors (nn) and next-nearest-neighbors (nnn) and may be either in high-spin (HS) or low-spin (LS) state. The interactions through the system are strongly dependent on the instantaneous distance between atoms and are magnetic and elastic in nature. Finite-size effects have been detected at finite temperature on the model. The thermal distortion of the lattice configuration due to lattice units displacements strengthened the thermal spin-transition that occurred. The generated numerical results are obtained by two-step Monte-Carlo (MC) simulations where used thermodynamic parameters allowed to establish a rich phase diagrams. Gradual and first-order transitions with thermally induced hysteresis phenomena have been observed. Near the thermal hysteresis loops, the model exhibits throughout relaxation curves, lattice configurations evolving through $2D$ -nucleation and growth processes that are enhanced with suitable values of the model parameters.

PACS numbers:

Keywords: Spin-Crossover compounds, Two-step Monte-Carlo simulations, phase diagrams, relaxation dynamics, Growth processes with $2D$ -nucleation

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I. INTRODUCTION

Molecular based materials as spin-crossover (SCO) solids and Prussian blue analogs (PBAs) [1] constitute a class of very promising materials with real opportunities of applications (in various domains of material science) as display and memory devices [1–4], multi-sensors [5–14], probes of contact pressure or shocks [15] as well as actuators [6, 16–18]. They are commutable solids with the presence of transition metal coordination which have an electronic configuration ranging between $3d^4$ and $3d^7$ (chromium, manganese, iron and cobalt) in octahedral symmetry, surrounded by Nitrogen atoms, called SCO complexes [1, 19–22]. In special conditions, they may exhibit a phase transition between the diamagnetic low-spin (LS) state and the paramagnetic high-spin (HS) state [23–25] under external stimuli such as light, pressure, temperature, magnetic and electric fields, etc [23–26]. The thermally induced spin-transition leads to both electronic and structural changes, often observed as a color and magnetic moment changes [1, 27, 28]. The system properties are strongly dependent on interactions between molecules. For weak interactions, the HS fraction changes smoothly with the temperature; whereas when they become strong enough, the system exhibits cooperative phenomena [29–31] which manifest through the existence of first-order transitions accompanied with thermal hysteresis. Then, the change in HS fraction becomes sharper and sharper with increasing interaction strength between molecules. Of course, the interaction in SCO solids is dominated by the variations of unit-cell volume and bond-length, that are considerably larger in the HS state.

The most common case studied in literature is of $Fe(II)$ -based SCO materials with $3d^6$ configuration where the total true spin equal to $S = 2$ and 0 in HS and LS states, respectively. The SCO phenomenon is the result of the redistribution of the electrons between the bonding t_{2g} and the antibonding e_g orbitals. In the diamagnetic ($S = 0$) LS state, only bonding orbitals are populated ($t_{2g}^6 e_g^0$), while in the paramagnetic ($S = 2$) HS state, the electronic configuration becomes ($t_{2g}^4 e_g^2$) according to the Hund's rule. The microscopic changes of the magneto-elastic properties of the SCO solids at the transition accompanied with large volume changes resulting from the constructive interferences of the molecular volume changes which deploy at long-range through elastic interactions. As well demonstrated in several works [29, 30, 32], the elastic interactions are at the heart of the existence of cooperative effects in SCO materials and play a crucial role in the existence of first-order transitions and

thermally induced hysteresis loops observed experimentally [29]. Novel properties [33–35], have been also detected for SCO solids, in particular the combination of magneto-elastic, photo-, thermo-chromic and photo-luminescence (PL) features [36–46] in the same material.

In this work, materials combining the spin-transition phenomenon with ferromagnetic interactions are investigated. Describing this particular SCO systems, we used the Blume-Emery-Griffiths (BEG) models [47–49] in which we accounted for the elastic and magnetic interactions [34, 50–62]. We demonstrate that the magnetic and elastic interactions generate tremendous changes in the spin-transition properties, leading to bring to light new and unprecedented non-linear behaviors of the HS fraction, n_{HS} . We study carefully, the competitions of the elastic-like interactions responsible for the existence of multi-step transitions and re-entrant phase transitions triggered by the magnetic interactions [52, 54, 55, 57, 58, 63–67]. A detailed study of the system properties allowed to establish a rich phase diagram [68, 69] in which the various system phases have been identified. Moreover, dynamical version of the present model based on a master equation treatment of the Hamiltonian, is also presented [70–72]. There, we studied the relaxation of the metastable high spin states at low temperature as well as the dynamical behavior at finite temperature in bistability regions.

The paper is organized as follows. In Section II, we define the Hamiltonian model of the system and presents its included interactions as magneto-elastic and electronic part which are responsible of the system structure and spin state modifications. Sec. III is devoted to the two step Monte-Carlo algorithm used on the spin state and for the displacements of the lattice sites. Sec. IV contains the discussions of the obtained results with the model parameters which are described in the Hamiltonian. In the last section, we conclude.

II. MODEL DESCRIPTION AND INTERACTION HAMILTONIAN

This work is inspired from the electro-elastic model of Boukheddaden et al. [50–55], designed to describe the thermally induced first-order transition in spin-crossover models accounting for their electronic and volume changes at the transition. The electro-elastic model was based on the study of a 2D lattice of SCO atoms coupled elastically through springs whose elastic constants and equilibrium distances depend on the spin states of the connected sites. In such a model, the spin-transition molecule is described with a fictitious spin, σ , whose values -1 and $+1$ associated to the low-spin (diamagnetic) and high-spin

(paramagnetic) states. As a matter of fact, this model does not include any ferromagnetic interactions between the spin states, and the HS spin state is then paramagnetic. Recent developments in the chemistry of spin-crossover materials and switchable solids [6, 73, 74], revealed new type of SCO materials which order magnetically in the HS phase (at low temperature). In these systems, the exchange (or super-exchange) interactions between the spin states in the HS state is then at work. Besides, the magnetic exchange interaction was introduced inside binuclear SCO complexes [75] together with an Ising-like interaction coupling between the binuclear units. To extend our previous two-states electro-elastic model to study the case of ferromagnetic SCO materials, we designed a spin-1 BEG model that takes into account electro-elastic interactions [50–53] between SCO units based on three-states fictitious spin description of a deformable lattice with square symmetry of size L . The spin variables at each lattice site can be in HS state with $S_i = \pm 1$ (magnetic state) or in LS state $S_i = 0$ (non-magnetic state). The degeneracy ratio between HS and LS states is defined by $g = g_{HS}/g_{LS}$, where g_{HS} and g_{LS} are the degeneracies of the HS and LS states, respectively. Here, we take $g = 150$, which leads to a molar entropy change at the transition, $\Delta S = R \ln g \simeq 41.7 \text{ J.K}^{-1}.\text{Mol}^{-1}$, which is in fair agreement with experimental data of literature [31, 76]. SCO molecules are assumed to elastically interact via springs and the lattice deformation is assumed to remain inside the plane (see Fig. 1). Thus, the topological structure of bonds between atomic sites will be conserved during the simulations. Since the elastic constant and equilibrium distances between lattice sites depend on the connected spin state values, the model is described by the following Hamiltonian:

$$H = H_{elec} + H_{magn} + H_{elas}, \quad (1)$$

where H_{elec} stands for the electronic contribution of ligand-field energy which is set to the value, $\Delta = 450 \text{ K}$, and entropy contribution $k_B T \ln(g)$ which stabilizes the HS state [47, 49, 77–80]:

$$H_{elec} = (\Delta - k_B T \ln g) \sum_i S_i^2. \quad (2)$$

Within these values of ligand-field and degeneracy ratio, the effective ligand-field energy cancels for the temperature value $T \simeq 90 \text{ K}$ which has the same order of magnitude of the transition temperature of SCO materials.

H_{magn} is the magnetic interaction between the spin states which is only between HS

species:

$$H_{magn} = - \sum_{\langle i,j \rangle} J(r_{ij}) S_i S_j, \quad (3)$$

and H_{elas} denotes the elastic part:

$$\begin{aligned} H_{elas} = & \frac{1}{2} \sum_{\langle i,j \rangle} A_{ij}(r_{ij})(r_{ij} - R_{eq}(S_i, S_j))^2 \\ & + \frac{1}{2} \sum_{\langle i,k \rangle} B_{ik}(r_{ik})(r_{ik} - R'_{eq}(S_i, S_k))^2, \end{aligned} \quad (4)$$

which accounts for nearest-neighbor (nn) and next-nearest-neighbor (nnn) interactions between the sites. The nnn interactions are introduced here to maintain the lattice stability with respect to shear distortion [50–53] particularly during the volume expansion / contraction accompanying the spin-transition along the transformation from the LS to HS phases / HS to LS phases. To take into account for the anharmonic effects of the lattice, leading to normal thermal expansion in the LS and HS phases, as well as for the difference of rigidity between the HS and LS phases (HS is less rigid than LS), the respective nn and nnn elastic constants, A_{ij} and B_{ik} are written under the following forms:

$$A_{ij}(r_{ij}) = A_0 + A_1 (r_{ij} - R_{eq}^{HH})^2 \quad \text{and} \quad B_{ik}(r_{ik}) = B_0 + B_1 (r_{ik} - \sqrt{2}R_{eq}^{HH})^2, \quad (5)$$

where $\langle i, j \rangle$ and $\langle i, k \rangle$ respectively run over the nn and nnn bonds, and R_{eq}^{HH} (resp. $\sqrt{2}R_{eq}^{HH}$) is the equilibrium lattice nn (resp. nnn) bond-length in the HS state. Thus, denoting by R_{eq}^{LL} (resp. $\sqrt{2}R_{eq}^{LL}$) the nn (resp. nnn) LS equilibrium bond-length, we clearly see from Eq. (5) that the nn (resp. nnn) elastic constant in the HS phase is $A_{HH} = A_0$ (resp. $B_{HH} = B_0$), while that of the LS state is $A_{LL} = A_0 + A_1 (R_{eq}^{HH} - R_{eq}^{LL})^2 > A_{HH}$ (resp. $B_{LL} = B_0 + 2B_1 (R_{eq}^{HH} - R_{eq}^{LL})^2 > B_{HH}$), which meets the constraints of rigidities imposed to two states. However, it is hard to connect a 2D model system to a 3D material. Indeed, some of the parameters like the ligand-field and the degeneracy have been chosen from the experiments. The ligand-field Δ , corresponds to the enthalpy change at the transition between the LS and the HS state, while the degeneracy ratio $g = g_{HS}/g_{LS}$ connects to the entropy change at the transition through the relation: $\Delta S = R \ln(g)$. This quantity is derived from calorimetric measurements, as stated above. For the other parameters, like elastic constants, magnetic interactions, it is really hard to connect them to experimental data, which result from 3D systems, in which in addition anisotropic effects may take place,

while here we treat the case of an isotropic 2D systems. Furthermore, at least the connection between the bulk modulus, Y , at 3D and the elastic constants in 2D can be approximated as, $Y \simeq A/a$, where A is the elastic constant of the 2D system and a is the lattice parameter. For the other parameters (nnn elastic constant) we do not have any experimental indication, and the strength of the magnetic interactions between the spins subsystem is taken here as a variable parameter allowing to tune the physical properties of the system.

In the magnetic part of Hamiltonian (1) whose expression is defined in Eq. (3), the exchange term, $J(r_{ij})$, represents the local magnetic coupling interaction between nn SCO sites and is written in the form:

$$J(r_{ij}) = J_0 - \alpha(r_{ij} - R_{eq}^{HH}), \quad (6)$$

in view to decrease the magnetic interaction during the lattice expansion. In Eq. (6), J_0 and α parameters are taken positive, so as to ensure ferromagnetic interactions between the SCO sites. As a result, the magnetic interaction in a lattice having the lattice parameter of the LS state is $J(r_{ij} = R_{eq}^{LL}) = J_0 + \alpha(R_{eq}^{HH} - R_{eq}^{LL})$, while it is equal to $J(r_{ij} = R_{eq}^{HH}) = J_0$ in the elastic HS phase. This point is important and will be discussed later when we examine the relaxation of photo-induced HS states.

Let us come back to the elastic part of the Hamiltonian (1) defined by Eq. (4) and discuss in more details the involved physical parameters. As stated above, the elastic constant, $A_{ij}(r_{ij})$ and $B_{ik}(r_{ik})$ correspond respectively to the nn and nnn bond stiffness constants whereas $r_{ij} = \|\vec{r}_i - \vec{r}_j\|$ (r_{ik}) is the instantaneous distance between nn (nnn) i and j (i and k) sites. As it emerges from Eq. (5), bond stiffness constants are taken as parabolic decreasing functions of the instantaneous distances, which then lead to quartic potentials. However, one may easily imagine other type of potentials [81, 82] satisfying the experimental condition of soft HS state and rigid LS state. Here, A_0 (B_0) and $A_1 > 0$ ($B_1 > 0$) are respectively the nn (nnn) harmonic and anharmonic contributions to the elastic energy.

The quantity, $R_{eq}(S_i, S_j)$ ($R'_{eq}(S_i, S_k)$) is the equilibrium distance between two nn (nnn) sites i and j (i and k), depending on the connected spin state. Since the spin configuration of two bounded sites can be HS-HS, HS-LS or LS-LS, we denote their corresponding bond-lengths as, R_{eq}^{HH} , $R_{eq}^{HL} = R_{eq}^{LH}$ or R_{eq}^{LL} , respectively. Thus, we obtain the following relations: $R_{eq}(+1, +1) = R_{eq}(-1, -1) = R_{eq}(+1, -1) = R_{eq}(-1, +1) = R_{eq}^{HH}$, $R_{eq}(+1, 0) = R_{eq}(0, +1) = R_{eq}(-1, 0) = R_{eq}(0, -1) = R_{eq}^{HL}$ and $R_{eq}(0, 0) = R_{eq}^{LL}$. Due to the

square symmetry of the lattice, the equilibrium distances, $R'_{eq}(S_i, S_k)$, between nnn sites, have been taken equal to those of nn sites multiplied by $\sqrt{2}$. According to these relations, it is straightforward to demonstrate that the spin dependence of the nn distance, $R_{eq}(S_i, S_j)$ can be obtained in a unique way as follows:

$$R_{eq}(S_i, S_j) = R_0 + 2R_1(S_i^2 + S_j^2) + R_2S_i^2S_j^2, \quad (7)$$

where $R_0 = R_{eq}^{LL}$, $R_1 = \frac{1}{4}(R_{eq}^{HH} - R_{eq}^{LL})$ and $R_2 = R_{eq}^{HH} + R_{eq}^{LL} - 2R_{eq}^{HL}$. Evidently, the R_0 represents the nn LS equilibrium distance, while R_1 corresponds to the misfit of lattice parameter between the HS and LS states, and $R_2 = 2\left(\frac{R_{eq}^{HH} + R_{eq}^{LL}}{2} - R_{eq}^{HL}\right)$ represents the difference between the centre of mass of HS and LS lattice parameter and that of HS-LS configuration. In the present work, we take for simplicity, $R_{eq}^{HL} = \frac{1}{2}(R_{eq}^{HH} + R_{eq}^{LL})$, which then gives $R_2 = 0$.

A preliminary analytical examination of the role of the bond stiffness in the energetic stabilization of the spin states helps in the understanding of the relevant parameters controlling the thermodynamic properties of this electro-elastic Hamiltonian. For that, we limit ourselves to the case of negligible nnn interaction and negligible anharmonic contributions. Using Eq. (7), Hamiltonian (1) is re-expressed in terms of the BEG Hamiltonian:

$$H = - \sum_{\langle i,j \rangle} J(r_{ij})S_iS_j + \sum_{\langle i,j \rangle} K(r_{ij})S_i^2S_j^2 + \sum_i D_iS_i^2 + \frac{A_0}{2} \sum_{\langle i,j \rangle} (r_{ij} - R_0)^2, \quad (8)$$

where the parameters $J(r_{ij})$, $K(r_{ij})$ and D_i are the local magnetic coupling interaction, the local quadrupolar interaction and the local crystal-field contributions respectively. The two first interaction parameters are given by:

$$J(r_{ij}) = J_0 - \alpha(r_{ij} - R_{eq}^{HH}) \quad \text{and} \quad K(r_{ij}) = 4A_0R_1^2, \quad (9)$$

and the effective local crystal-field writes:

$$D_i = \Delta - k_B T \ln(g) + 2A_0R_1 \left[zR_1 - \sum_{j=1}^z (r_{ij} - R_{eq}^{LL}) \right] \quad (10)$$

The fact that the quadrupolar interaction K , which is here positive and exclusively short-range, indicates that this term stabilizes nn spin configurations $S_i = 0$, $S_j = \pm 1$ or

$S_i = 0, S_j = 0$ which means HS-LS or LS-LS configurations. In contrast, the magnetic term stabilizes HS-HS (i.e. $\pm 1-\pm 1$) neighboring sites. On the other hand, the effective crystal-field acting on a spin site now depends on the elastic field created by the neighbors which acts as an internal pressure. The inspection of the elastic contribution, $2A_0R_1 \left[zR_1 - \sum_{j=1}^z (r_{ij} - R_{eq}^{LL}) \right]$ to the effective crystal-field shows that it is positive when $r_{ij} = R_{eq}^{LL}$ (LS bond-length) thus stabilizing the LS state and becomes negative for $r_{ij} = R_{eq}^{HH}$ (HS bond-length) stabilizing the HS state. This behavior of the elastic field establishes a direct synergy between the entropic effects of the degeneracy and the elastic interactions.

III. THE TWO-STEP MONTE-CARLO ALGORITHM

A planar lattice of square symmetry with $N = L_x \times L_y$ SCO sites is considered with free boundary conditions. The simulations are alternatively executed on spin and position variables in a two-step strategy. The metropolis algorithm is considered for the spins and lattice positions update procedure (sites displacements). Then, the stochastic algorithm is performed in the following way: for a site (i, j) randomly selected, with spin $S_{ij} = \pm 1, 0$ and position, r_{ij} , a new spin value S'_{ij} (such that $S_{ij} \rightarrow S'_{ij} = \pm 1, 0$ ($S_{ij} \neq S'_{ij}$)) is set without position change. This spin change is accepted or rejected by the usual Metropolis criterion. Whatever the result (acceptance or rejection) the lattice whole is relaxed mechanically by a slight motion of nodes (selected randomly) with a quantity $\delta u = 0.03$ (in any direction: $u = x, y$) which is much smaller than the distance between the spin states. The lattice relaxation is also performed following a Monte Carlo technique at fixed spin configuration. The procedure of the lattice relaxation is once repeated for each spin flip. Afterwards, a new spin site will be selected randomly and so on, etc. Once all nodes of the lattice are visited for the spin change, we define such step as the unit of the Monte Carlo step and denoted "MCS". Physical quantities of interest are calculated in the steady state with $N_S = 10^5$ MC steps per site for the spin-flip dynamics and for each spin-flip attempt, all SCO units displacements are once attempted (one Monte-Carlo cycle). Specifically, a spin variable and its position are randomly selected within the possible projections with a uniform distribution. About $N_E = 2 \times 10^4$ MC steps per site are considered for thermal equilibration in the spin-flip dynamics and then discarded from the averaging procedure. Three to five independent runs are performed on each MC process in view to get smooth data. The lattice magnetization

is calculated as follows:

$$m = \langle S \rangle = \frac{1}{N} \sum_{i=1}^N S_i. \quad (11)$$

The n_{HS} fraction is evaluated as follows:

$$n_{HS} = \langle S^2 \rangle = \frac{1}{N} (N_+ + N_-), \quad (12)$$

where N_+ and N_- are numbers of spins in the up and down states respectively. The magnetic critical temperature, T_C , is defined in the present work as the temperature associated to the peak in the magnetic susceptibility curve when the magnetization is continuously decreasing to vanish. The magnetic susceptibility is calculated by the formula:

$$\chi = \langle \langle (\bar{S})^2 \rangle - m^2 \rangle, \quad (13)$$

where \bar{S} is the averaged system magnetization at a given step of the simulation and $\langle . \rangle$ denotes a statistical average over the $(N_S - N_E)$ MC steps. Another transition temperature of interest, $T_{1/2}$, is that of the spin-transition phenomenon which occurs when the HS fraction, n_{HS} , is equal to 1/2. We also calculate the average intermolecular distance $\langle d \rangle$, between nn SCO sites that provides information about the lattice "volume" change along the spin-transition. Its expression is given by:

$$\langle d \rangle = \frac{\sum_{\langle i,j \rangle} \sqrt{(x_j - x_i)^2 + (y_j - y_i)^2}}{(L_x - 1)L_y + (L_y - 1)L_x}, \quad (14)$$

with i and j run $[1, L_x]$ and $[1, L_y]$ respectively.

IV. RESULTS AND DISCUSSIONS

The present work, uses as far as possible, realistic model parameters values, already derived in previous electro-elastic modeling of SCO materials by one of the authors [50–56]. The chosen ligand-field energy value, $\Delta = 450K$, leads to a molar enthalpy variation at the transition $\Delta H \simeq 3.7 \text{ kJ.Mol}^{-1}$, while the entropy change at the transition, already evaluated to $\Delta S \simeq 41.7 \text{ J.K}^{-1}.\text{Mol}^{-1}$, gives a spin-transition temperature, $T_{1/2} = \frac{\Delta H}{\Delta S} = \frac{\Delta}{k_B \ln g} \simeq 90 \text{ K}$.

As well, the values of equilibrium distances between two nn sites, which depend on the spin configuration of linked sites, are taken as follows: $R_{eq}^{HH} = 1.2 \text{ nm}$, $R_{eq}^{LL} = 1 \text{ nm}$, $R_{eq}^{HL} = \frac{1}{2}(R_{eq}^{HH} + R_{eq}^{LL}) = 1.1 \text{ nm}$. In view of the square 2D symmetry of the lattice, the

nnn equilibrium distances are simply chosen as: $R_{eq}^{HH} = \sqrt{2}R_{eq}^{HH}$, $R_{eq}^{LL} = \sqrt{2}R_{eq}^{LL}$ and $R_{eq}^{HL} = \sqrt{2}R_{eq}^{HL}$ for the three possible electronic configurations. It is worth mentioning that the value of the lattice misfit, $(R_{eq}^{HH} - R_{eq}^{LL})$ is taken a little bit high in order to enhance the lattice distortions for the small lattice sizes, investigated in this study.

The effect of the elastic intermolecular interactions on the SCO transition is investigated by considering different values of the elastic constants. Indeed, the variation of the equilibrium intermolecular distance and bond stiffness upon the LS to HS transition results in volume and bulk modulus changes, which are experimental features of the spin-transition in SCO solids [83–89]. Here, we take $A_0 = B_0$ in the range 500 to 10^4 K.nm^{-2} , leading to an order of magnitude of bulk modulus $E \simeq A_0/R_{eq}$ in the range 0.1-2 GPa , in quite good agreement with bulk modulus of polymeric materials. The anharmonic contributions to the elastic constants are, for simplicity, taken as $A_1 = B_1 = 10A_0$. However, it is important to notice that their contributions, $A_1(r_{ij} - R_{eq}^{HH})^2$, to the total elastic stiffness is maximum in the LS state and is equal to $A_1(R_{eq}^{LL} - R_{eq}^{HH})^2 = 200 \text{ K}$ (for $A_0 = 500 \text{ K.nm}^{-2}$) which then represents 40% of the total elastic energy.

Another new contribution with respect to previously published electro-elastic models concerns the magnetic interaction between the SCO units, represented in Hamiltonian (3) by the local exchange interaction $J(r_{ij})$. The values of the constant part, J_0 , of this term are selected in the range $J_0 = 30\text{-}100 \text{ K}$, which leads in a simple Onsager 2D model lattice to magnetic transition temperatures in the range 85-226.90 K . The parameter α , representing the magneto-elastic coupling in this model, is taken in the range of $\alpha = 0\text{-}700 \text{ K.nm}^{-1}$ values. The total magnetic energy reaches its maximum value, when all spin states are LS and lattice bond-lengths are equal to those of the LS lattice ($r_{ij} = R_{eq}^{LL}$). In this case, the magneto-elastic contribution exchange interaction, $J = J_0 - \alpha(r_{ij} - R_{eq}^{HH})$ takes its maximum value, 20 K which still remains small compared to J_0 for $J_0 = 50 \text{ K}$ and $\alpha = 100 \text{ K.nm}^{-1}$.

A. Finite-size effects in gradual spin- and magnetic-transitions

The application of the two-step MC procedure enables us to estimate steady state finite-size effects on various physical quantities, namely, the HS fraction, n_{HS} , the net magnetization m , the magnetic susceptibility χ and the average intermolecular distance, $\langle d \rangle$, between nn SCO sites, as well as spin-spin correlation C . Various system sizes, 8×8 , 12×12 ,

16×16 and 16×24 SCO units are selected and investigated. Corresponding numerical results are illustrated in Fig. 2. The simulations are performed with the value of the nn harmonic elastic interaction, $A_0 = 2000 \text{ K.nm}^{-2}$, for which we do not expect a first-order spin-transition, but rather a continuous transformation from LS to HS.

In panel (a), the temperature dependence of the HS fraction n_{HS} , is presented for different system sizes. The set of obtained curves shows a continuous gradual transition between the values $n_{HS} = \langle S^2 \rangle = 0$ (LS state) and $n_{HS} = 1$ (HS state). It evidently appears that finite-size effects are almost negligible for lattice sizes beyond 16×16 . Panel (b) displays the net magnetization, m , which shows a re-entrant-like behavior. Indeed, m is zero in the temperature interval 0-50 K and then suddenly increases, goes through a maximum, the height of which increases with system size, and finally falls down at high temperatures, i.e. in the HS phase. The final value of m decreases as the system's size increases, indicating that in the thermodynamic limit this value will be zero, and the system will reach the paramagnetic phase. These observations insure that in the thermodynamic limit, the magnetization will reach its maximum value, not necessarily, $m = 1$, and its non-zero value will only prevail in a narrow temperature range. These observations suggest that at low and high temperatures, the system will be globally non-magnetic. Indeed, at low temperatures, the LS state ($\langle S^2 \rangle = 0$ and $\langle S \rangle = 0$) is stabilized by the ligand-field and the elastic interactions, and so one gets $m = 0$ and $n_{HS} = 0$. This is a strictly diamagnetic phase, where the SCO lattice is exclusively populated by spins of values 0. In the high temperature limit, the states $S = +1$ and $S = -1$ are equally populated, and the HS state is favored which leads to stabilize the paramagnetic state characterized by, $m = 0$ and $n_{HS} = 1$ for very large systems. Between the two previous phases, an totally- or partially-ordered phase with $m \neq 0$ and $n_{HS} \neq 0$ emerges (see Figs. 2a,b). Here, a ferromagnetic phase appears embedded in two non-magnetic phases. The above observations are strengthened by the computation of the magnetic susceptibility curves, illustrated in Fig. 2c. Two peaks can be observed for each system, except for the low sized one. The first peak appears after a very sharp jump of $\chi(T)$ and is attributed to the spin-transition which occurs at about $T = 72 \text{ K}$ for the 16×24 system. A direct finite-size analysis of the behavior of the first peak height χ_{max} with system size formally given by the square root of the system volume (number of SCO units) is performed (see inset of Fig. 2c). Calculations yield a behavior of the form $\chi_{max} \simeq N^{0.5\delta}$. The extracted exponent from a log-log plot is $\delta = 1.75 \pm 0.06$, which value is close to the $2D$

system. This scaling result physically indicates that the peak is associated to a macroscopic instability in the system that results from microscopic cooperative phenomena to which most SCO units contribute. This instability is of first-order kind and is accompanied by a hysteresis phenomenon. The associated pseudo-transition temperature is slowly decreasing with increasing system size showing some convergence. It is important to mention that the critical exponent is "measured" on the magnetic subsystem which is, of course, coupled to the SCO elastic lattice through the magneto-elastic interaction. However, the effect of the SCO transition is to drive the system from the diamagnetic ($S = 0$) to magnetic state ($S^2 = +1$) through first-order or gradual transformation (Figs.2 and 3). But then, when the magnetic order is generated, the SCO elastic interactions play a negligible role in the system's behavior (the lattice parameter becomes almost that of the HS and does not change a lot). As a result, the magnetic transition from the ferromagnetic to the paramagnetic state, which takes place at higher temperature than the SCO transition mainly follows the behavior of that of an Ising model, although the "exchange" interaction J slightly depends on the distances as $J(r_{ij}) = J_0 - \alpha(r_{ij} - R_{eq}^{HH})$. However, as we explained above, in the HS region, one has $\langle r_{ij} \rangle \simeq R_{eq}^{HH}$, and so the effect of the long-range interactions on the magnetic subsystem remain negligible. That is the main reason for which the same critical exponent as that of the 2D Ising model is found in these simulations.

The second less sharp peak is attributed to a second-order phase transition taking place in the HS state between the ferromagnetic phase at intermediate temperatures and the paramagnetic disordered phase that prevails at high temperature. For the 16×24 system, the ferromagnetic phase exists between temperatures associated to both peaks of χ which are estimated to $72 K$ and $93 K$. The order-disorder transition temperature, $T_C \simeq 93 K$ well corresponds to the expected Onsager critical temperature of a 2D Ising system, $T_C = 2.269 (J_0 - \alpha(\langle d \rangle - R_{eq}^{HH}))$. Using these values, the critical temperature is estimated using Onsager formula, $T_{Ons} = 2J / \ln(1 + \sqrt{2})$ which gives $T_{Ons} = 2.269J_0 = 113.4 K$ in the case of a perfect HS system, for $J_0 = 50 K$. On the other hand, at the maximum value of χ , the corresponding HS fraction value is $n_{HS} \simeq 0.9$, (the magnetization peaks at $m \simeq 0.6$) indicating that the present ferromagnetic phase is only partially ordered. Consequently, the ferromagnetic phase of Fig. 2b must be seen as a diluted phase containing about 10% of diamagnetic LS phase, randomly distributed. Thus, the critical transition temperature, is lower than that of the pure saturated HS phase and can be estimated in a simple attempt as,

$T_{Ons}^{dilut} = 0.9T_{Ons} \simeq 103 \text{ K}$. It is however important to mention that the ferro-paramagnetic transition temperatures, estimated from the MC simulations, crucially depends on the system size. Thus, for a finite system, the critical temperature is always lower than that of Onsager, to which it connects through the following relation, $T_C = T_{Ons}/(1 + \frac{5}{4\sqrt{N}})$ [90], where N is the system "volume". According to these developments, one can evaluate analytically using, for the case 16×16 system, the expected ferromagnetic to paramagnetic transition temperature as $T_C = T_{Ons}^{dilut}/(1 + \frac{5}{4\sqrt{N}}) \simeq 95 \text{ K}$, which is in excellent agreement with the value $T_C = 93 \text{ K}$ emerging from the simulations.

One crucial parameter of the model is the average intermolecular distance, $\langle d \rangle$, between nn SCO molecules. Reported in Fig. 2d, its behavior with temperature is quite similar to that of n_{HS} and finite-size effects are also found negligible on this quantity beyond the 16×16 system size. The linear increase of intermolecular distance, $\langle d \rangle$, in the HS and LS phases is due to thermal expansion, caused by the anharmonic (quartic) elastic term of the Hamiltonian. Due to the form of the anharmonic contribution ($A_1 (r_{ij} - R_{eq}^{HH})^2$) to the nn elastic constant, which is stronger in the LS spin state ($r_{ij} = R_{eq}^{LL}$) and almost negligible in the HS state ($r_{ij} = R_{eq}^{HH}$), the slope of the curve $\langle d \rangle (T)$ is higher in the LS phase. According to this behavior, the thermal expansion coefficient for the nn bond-length, defined as $\alpha_T = d(\ln \langle d \rangle)/dT$, leads to the value, $6.4 \times 10^{-4} \text{ K}^{-1}$, which is found the same for all investigated system sizes. This value strongly depends of the anharmonic elastic constant A_1 which was taken quite high in the simulations ($A_1 = 10A_0$) in order to magnify this phenomenon. In the temperature interval 60-90 K , the intermolecular distance, undergoes a rapid increase in the same region of first-order transition as that of the HS fraction (see panel a) and finally saturates at high temperatures. This thermal behavior of $\langle d \rangle$ leads to an important remark concerning the magnetic properties. Indeed, the total exchange like interaction, J , depends on the nn distance between the SCO sites, and therefore at fixed temperature, T , its average value, $\langle J \rangle = J_0 - \alpha (\langle d \rangle - R_{eq}^{HH})$ is clearly temperature-dependent. This makes the study of the magnetic subsystem more complex than thought, and in the same time this fact makes the problem extremely close to the previous BEG studies [47, 78–80] in which all interacting parameters, including magnetic exchange, were assumed to be linearly depend on temperature.

The fact that a sharp transition takes place exactly in the same region for the electronic state, that is the HS fraction parameter (see panel a), and the structure, that is the lattice

parameter, is a key MC result of the model which reproduces experimental observations on SCO solids at the spin-transition. The correlation between n_{HS} and $\langle d \rangle$ is also explored by computing n_{HS} as function of $\langle d \rangle$ (see inset of Fig. 2d) as the temperature varies. Corresponding data collapse for different system sizes in a straight line of slope 0.2 nm , establishing an undoubtedly evident correlation between n_{HS} and $\langle d \rangle$. The thermal behavior of the spin-spin correlation function $C(T) = \langle S_i S_j \rangle$ has been also examined with system size. The results (not reported) are similar to the one observed in Fig. 2b. Less finite-size effects are obtained at low and high temperatures than in Fig. 2a. In these temperature ranges, curves for different system sizes collapse.

B. Effect of the harmonic elastic constant A_0

Now, we study the effect of the model parameter values on the system. For that, since large scale computing properties of the model is demanding in simulation time, the 16×16 system is selected to predict qualitatively the thermal behavior of magnetization m , HS fraction n_{HS} , magnetic susceptibility χ and average intermolecular distance $\langle d \rangle$, as function of the elastic constant A_0 . Fig. 3 summarizes the system's behavior for three values of this constant: $A_0 = 1000, 4000$ and 8000 K.nm^{-2} . One sees that the HS fraction, n_{HS} (see panel a), changes from gradual to sharp discontinuous transition with unchanged transition temperature, $T_{1/2} \sim 69 \text{ K}$. This behavior can be well understood, since the transition temperature between the LS and HS states involves only a change of the total effective ligand-field, whose elastic part vanishes at the transition. Therefore, the transition temperature at which the system switches between the LS and HS states, only depends on Δ , J_0 and g . Panels (b) and (c) show the magnetization, m and the susceptibility, χ which also change from a continuous transition character to discontinuous when values of the elastic constant A_0 increases. Thus, for $A_0 = 4000$ and 8000 K.nm^{-2} , the magnetization jumps from 0 to 0.9 exactly at the SCO transition and then vanishes following a second order-disorder transition whose critical temperature, T_C , depends on A_0 , as well indicated by the shift of the broad maxima of the susceptibility χ (see panel c). This behavior highlights the effect of the elasticity of the material on the magnetic properties. Finally, panel (d) shows that the average intermolecular distance, $\langle d \rangle$, is influenced by the change of A_0 mainly in the LS state where the LS lattice distance $\langle d \rangle = 1 \text{ nm}$ is stabilized for high A_0 while

the transition transforms from gradual to first-order, in agreement with $n_{HS}(T)$ behavior.

C. Effects of the magnetic coupling J_0 and the magneto-elastic coupling constant

α

As for Fig. 3, quite similar tendencies are observed for increasing values of the coupling constant J_0 at fixed A_0 value (see Fig. 4). However, one can remark the existence of notable differences between the effects of A_0 and J_0 . First of all, increasing J_0 from 30 to 100 K shifts downward the spin-transition temperature, as indicated in Fig.4(a), and so the exchange coupling J_0 stabilizes the magnetic HS spin phase while giving a sharper character to the spin-transition, as A_0 does. It is interesting to notice that the SCO transition temperature can be determined analytically in this model. At the switching temperature between the LS and HS states, free energies of HS and LS phases must be equal. Let us denote by P_{HS} and P_{LS} the probabilities of occupying HS and LS sites, respectively. Their general expressions are given as, $P_{HS} = \Omega_{HS}e^{-\beta E_{HS}}$ and $P_{LS} = \Omega_{LS}e^{-\beta E_{LS}}$, where Ω is the electronic degeneracy of the spin state ($\Omega_{HS} = 2$ and $\Omega_{LS} = 1$) and E_{HS} (resp. E_{LS}) is the energy per site in the HS (resp. LS) state. At the transition, one has $P_{HS} = P_{LS}$. On the other hand, the transition takes place between LS and HS ordered phases (their mixing entropy's are equal to zero). Moreover, the elastic energies of HS and LS phases are also zero (see Eq. (4)), and therefore, the energies of the HS and LS phases are simply given by $E_{HS} = D_{eff} - J_0$ (where $D_{eff} = \Delta - k_B T \ln(g)$) and $E_{LS} = 0$, respectively. At the transition we then have, $e^{-\beta[(\Delta - k_B T_{1/2} \ln 2g) - J_0]} = 1$, which leads to the transition temperature, $k_B T_{1/2} \simeq \frac{\Delta - J_0}{\ln 2g} = 72$ K for $J_0 = 40$ K, which is in excellent agreement with that of MC simulations, derived from Fig.4(a) for $n_{HS} = 1/2$: when a half of the system has switched from the LS to the HS state.

In this problem, the system exhibits two magnetic transitions. The first-one, strongly correlated to the SCO transition takes place between the diamagnetic state ($\langle S^2 \rangle = 0$ and ferromagnetic state ($\langle S^2 \rangle = 1$). The second ferromagnetic-paramagnetic order-disorder transition takes place at higher temperature in the present studied cases. To observe a crossover between the critical exponent of 2D Ising model and that of mean-field universality class, we must have a long-range magnetic coupling between the spin states along the ferro to paramagnetic transition. In other words, there must be a strong interference between the magnetic transition temperature and the SCO temperature. If these two temperatures are

very close, then the two transitions will interfere and as a result the magnetic interaction $J(r_{ij})$ will strongly depend on the lattice parameter in the temperature region where the magnetic phase transition take place between the ferromagnetic and the paramagnetic HS states. Although interesting, we believe that this type of study merits a specific work.

The shift of the SCO transition can be evaluated through the relation $T_{1/2} = \frac{\Delta - J_0}{k_B \ln 2g}$ in the domain where the second-order and SCO-transition temperatures are very close regarding to J_0 values (e.g. for $J_0 = 30 K$, $T_c = 90 K$ and $T_{1/2} = 75 K$ with MC simulations) and the exact relation yields $T_{1/2} = 73.63 K$. This estimation is in fair agreement with the MC simulations of Figs. 4a,b. Beyond that, the obtained result leads to a lowering of the first-order transition temperatures ($T_{1/2} = 52 K$ for MC simulations) by of $61.36 K$ and with $T_c = 204 K$, for high second-order transition temperature, when J_0 is increased to $100 K$. As such, this leads to have non-valid relation between $T_{1/2}$ and $\frac{\Delta - J_0}{k_B \ln 2g}$. This effect is also found in the magnetic transition (see Figs. 4c), which also shows a huge effect of J_0 on the second-order phase transition, as expected from theory of 2D Ising systems. Indeed, a clear saturation of the magnetization m at high temperatures and an increasing of the domain of the ferromagnetic phase with J_0 which is a common feature in Ising systems [49, 77, 78]. Here, the HS units are created and interact magnetically in the system. Overall, in Fig. 3 we demonstrated that an enough strong harmonic elastic coupling, A_0 , induced a first-order SCO (on $n_{HS}(T)$) triggers a first-order transition on the magnetization, $m(T)$, from the LS diamagnetic state to an ordered (or partially-ordered) ferromagnetic state. Here, we also demonstrate that the opposite effect is also possible, since an increasing magnetic interaction, J_0 , induces a first-order SCO transition. This interplay between the elastic and the magnetic interactions is even more flagrant in the curves of Fig. 4d, which present significant effect of J_0 on the average intermolecular distance, $\langle d \rangle$, which is a purely structural quantity. Here, we see that the slopes of $\langle d \rangle (T)$, in the HS phase change with respect to J_0 , which means that even the thermal expansion coefficient ($\frac{d \ln \langle d \rangle}{dT}$) depends on J_0 values. This proves that the magneto-elastic interaction introduced in this model is very efficient and allows a strong coupling between the magnetic and the structural properties of the lattice. Thus, the average intermolecular distance, $\langle d \rangle$, from the LS diamagnetic state to an ordered (or partially-ordered) ferromagnetic state is a relevant parameter that shows the relationship between the system volume change and the magneto-elastic interaction. In addition, as in Fig. 4, similar tendencies are observed for increasing values of the magneto-elastic coupling α at

fixed J_0 and A_0 values (see Fig. 5). For increasing α values, one gets first- and second-order transitions where the former coincides to the equilibrium spin-transition temperature ($n_{HS} = 1/2$). All transition temperatures shifted to lower values with increasing α value as depicted in the inset of Fig. 5a. For $J_0 = 60 K$ and $A_0 = 1000 K.nm^{-2}$, Dia-Ferro and Ferro-Para-magnetic characters of the transition are found from thermal behaviors of the thermodynamic quantities (HS fraction n_{HS} , magnetization m and magnetic susceptibility χ).

D. Phase diagrams

It should be interesting to devise the temperature phase diagram of the model, relying on the behavior of the HS fraction, and the magnetic susceptibility. The results as functions of A_0 and J_0 , for two selected values of J_0 (panels a and b) and for two selected values of A_0 (panels c and d), respectively, are presented in Fig. 6. It is observed that the high temperature phase is a disordered phase, and the low temperature one is a diamagnetic phase. The intermediate phase is the ferromagnetic phase, that is separated from the diamagnetic phase by continuous spin-transitions at low values of A_0 (or J_0 , respectively), and by first-order transitions at higher values of both parameters. It is important to notice that the model does not exhibit tricritical points for the selected values of J_0 (or A_0 , respectively), contrarily to observations done in our previous works, where only spin-flip dynamics are considered. This absence could be a finite-size effect. From Figs. 6a,b, it emerges that the transition lines decrease as function of A_0 , with the presence of a sharp kink in the T_C -lines at $A_0 R_1^2 = 10$ and $2.5 K$, respectively in panels (a) and (b). Beyond these kinks, the spin-transition occurs through a first-order transition at low temperatures, where discontinuities are observed in the thermal behaviors of the order-parameters. In this range of $A_0 R_1^2$, the transition lines increase and reach their limit values. With increasing J_0 value, one can remark that the domain of the ferromagnetic phase increases as in most Ising-like ferromagnetic systems as previously stated, and the onset temperature for the appearance of the first-order transition decrease. This remark is also observed in Figs. 6c,d, where the transition lines decrease slightly when J_0 increases, with appearance of a sharp kink at about $J_0 = 50 K$ (panel c), and $J_0 = 40 K$ (panel d), in the T_C -lines. From these values of J_0 , the spin-transition lines are first-order, and may decrease with J_0 , whereas the T_C -lines undergo a rapid increase,

resulting in the increase of ferromagnetic phase domain.

E. Thermal hysteresis behaviors of the system

At the vicinity of first-order transitions, hysteresis phenomena are observed. Here a 32×32 system is considered and the calculations are proceeded as follows. The temperature is raised from 1 K to 130 K with an increment of 1 K. When 130 K is reached, the simulations continued to 1 K with a temperature step of -1 K. The hysteresis cycles achieved are illustrated in Fig. 7 for varying values of the parameters A_0 (panel a) and J_0 (panel b) and selected values of other parameters that are indicated in the panels. It is observed that when the value of A_0 is raised, the switching temperature of the upward branch $T_{1/2\uparrow}$ increases while that of the downward branch $T_{1/2\downarrow}$ decreases (see Fig. 7a). As a consequence, the cycle area increases with A_0 . Interestingly, the center of the cycle evidently remains almost constant in this A_0 range, in good agreement with the previous analytical predictions which indicated that the transition temperature at equilibrium does not depend on the harmonic elastic constant, A_0 . On the contrary, increasing values J_0 shift the hysteresis loop to low temperatures with a decrease of the associated $T_{1/2\uparrow}$ and $T_{1/2\downarrow}$ values and a clear saturation of the lattice by HS units at high temperatures (see Fig. 7b). The magnetization corresponding to the case of $J_0 = 100$ K, as displayed in the inset of Fig. 7b, shows also hysteresis behavior with a clear saturation in the HS phase. Figs. 8a,b show the behavior of the limiting transition temperatures $T_{1/2\uparrow}$ and $T_{1/2\downarrow}$ of the hysteresis loops as well as the associated equilibrium temperatures, defined as $T_{1/2} = \frac{1}{2}(T_{1/2\uparrow} + T_{1/2\downarrow})$ as function of the harmonic elastic constant, A_0 , and magnetic interaction J_0 , respectively. The corresponding widths $\Delta T = T_{1/2\uparrow} - T_{1/2\downarrow}$ are also monitored when A_0 and J_0 increase. In panels (a) and (c) of this figure, at low values of A_0 and for $J_0 = 50$ K, $\Delta T = 0$ K and only critical hysteresis cycles can be observed. There, the SCO lattice presents only gradual SCO transition and the magnetic subsystem, exhibits only second-order phase transitions, where $T_{1/2\uparrow} \simeq T_{1/2\downarrow} \simeq T_{1/2}$. This is in fact the case for $A_0 = 10^3$ K.nm⁻² where one maximum is found for the response function χ in Fig. 3c. With increasing A_0 , one can see from this figure that a second maximum appears in the low temperature range. In this case, jumps are observed in the behavior of m , n_{HS} and χ and thermal hysteresis loops take place, as we have already explained. From the above, the existence of a critical value

of the interaction parameter A_0 is obvious (see Figs. 8a,c). Close to this critical point, the upward borderline is slightly curved. This feature may account for the finite value of the temperature sweeping rate (kinetic effect) [50, 77]. For $J_0 = 80 \text{ K}$ (Figs. 8b,c), the same behaviors are obtained with a decrease of the transition temperatures ($T_{1/2\uparrow}$, $T_{1/2\downarrow}$ and $T_{1/2}$) and an increase of hysteresis loop width as shown in Fig. 7b. One also remarks that from the critical point, the hysteresis loop width increases gradually with the parameter A_0 and an almost straight lines are obtained (see Fig. 8c). We now turn to the study of the spatio-temporal features of the SCO transformation obtained with this model. At this end, some snapshots of transient states have been taken along the thermal hysteresis loop in heating and cooling processes of Fig. 7a for the elastic constant value, $A_0 = 8.10^3 \text{ K.nm}^{-2}$. In this figure, one remarks that the transition from the LS to HS state (LS \rightarrow HS) occurs around $T_4 = 75 \text{ K}$ on heating and from the HS to LS state (HS \rightarrow LS) around $T_8 = 55 \text{ K}$ on cooling. Both processes proceed via nucleation phenomena with domain growth. The obtained results are summarized in Fig. 9 which shows, in addition to the nucleation and growth process of the HS (red/blue) and LS (green) spin domains in the model accompanied by the volume (here surface) change at the transition process, the clear occurrence of the magnetic order-disorder transition. As reported in Refs. [50–53, 82, 91–95] one can observe that the nucleation and growth processes of spin domains start from edges and corners for both HS \rightarrow LS [Fig. 9: F(T_6)-A(T_1)] and LS \rightarrow HS [Fig. 9: A(T_1)-F(T_6)] transitions. The growing domains propagate towards the center of the lattice and then merge. During HS \rightarrow LS transformation, LS domains grow and finally combine together to extend to the whole system. Domain growth occurs in the diagonal directions and a few one appears somewhere at the edges (see right panels of Fig. 9). The onset of such inhomogeneous structures was reported in Fig. 1 of Ref. [96] during the domain wall propagation observed by optical microscopy [17, 48, 49, 72, 73, 77, 93, 96–109]. Following the process in heating from LS to HS phase, we also find local clusters of HS molecules (blue and red dots) around the corners, but in contrast to the case of the cooling branch, a large homogeneous region appears (see left panels of Fig. 9) as is observed with periodic boundary conditions (PBC) thus meeting the previous investigations of Nishino et al. [91], who pointed out the crucial role of the surface in the emergence of macroscopic domains nucleation in the elastic models. It is important to mention in passing, that years ago an hybrid model combining short-range Ising coupling and elastic long-range interactions was proposed by Nakada et al. [110] who

demonstrated that an inhomogeneous configuration (lattice and spin degrees of freedom) are also observed at critical temperature T_c when the SCO atoms interact in a lattice with periodic boundary conditions.

A possible reason for this difference on cooling and heating processes originates from the energy and entropy gain. In the cooling process at low temperatures, the energy stability is more important than the entropy gain and the nucleation from the corner is the most favorable. However, in the heating process at high temperatures, the entropy gain becomes more important and the configuration may change uniformly, which can be seen in the inner part of the system. This obviously indicates that the system, once in the saturated HS phases, the HS units interacted magnetically.

Furthermore, following the same procedure as that developed in Ref. [50], the nucleation and growth processes from the corners in our model can be explained by simple energetic considerations. During HS \rightarrow LS transition for example, let us start from a lattice with a saturated HS states and consider a nucleus made of a single LS site. The energy cost associated with the creation of an LS nucleus at the corner, edge and center of the HS lattice defined by $\Delta E = E(LS) - E(HS)$ reads as:

$$\Delta E_{Corner}(HS \rightarrow LS) = -(\Delta - k_B T \ln(g)) + 2J_0 + 4(A_0 + B_0)R_1^2 \quad (15)$$

$$\Delta E_{Edge}(HS \rightarrow LS) = -(\Delta - k_B T \ln(g)) + 3J_0 + 2(3A_0 + 4B_0)R_1^2 \quad (16)$$

$$\Delta E_{Center}(HS \rightarrow LS) = -(\Delta - k_B T \ln(g)) + 4J_0 + 8(A_0 + 2B_0)R_1^2 \quad (17)$$

The analysis of these equations clearly shows that while the system wins electronic energy (especially at very low temperature) during the spin-flip from HS to LS, it also faces to an energy barrier originating from the magnetic and the elastic interactions, whose contributions can be easily identified in the previous equations. The interesting point here is that magnetic and the ligand-field energies compete (in the case of ferromagnetic interactions) and it is clearly seen that the magnetic interactions stabilize the HS phase, by increasing the energy barrier. Moreover, both of these contributions increase when going from corner to edge and then to a bulk site. As a result, the probability of appearance of a LS state along the cooling process ($\sim e^{-\beta\Delta E}$) is higher for corner atoms. This justifies the nucleation and growth of spin domains from corner of lattice. For LS \rightarrow HS transition, similar considerations have been developed. We start from a LS lattice in which we flip a corner, edge or central site

form LS to HS. The following energy barriers are found for each case as:

$$\Delta E_{Corner}(LS \rightarrow HS) = \Delta - k_B T \ln(g) + 4(A_0 + B_0)R_1^2 + 64(A_1 + 2B_1)R_1^4 \quad (18)$$

$$\Delta E_{Edge}(LS \rightarrow HS) = \Delta - k_B T \ln(g) + 2(3A_0 + 4B_0)R_1^2 + 32(3A_1 + 8B_1)R_1^4 \quad (19)$$

$$\Delta E_{Center}(LS \rightarrow HS) = \Delta - k_B T \ln(g) + 8(A_0 + 2B_0)R_1^2 + 128(A_1 + 4B_1)R_1^4 \quad (20)$$

in which the elastic energy part remains unchanged because of its positive character with a weak additional term in R_1^4 , while the ligand-field contributions changed its signs and the magnetic part vanished. Adopting the same energetic reasoning, here again, the energy barrier at the corner is the smallest one and so the nucleation will start from the corner sites. Compared with the cooling process, the heating one shows large thermal fluctuations which favor the probabilities of nucleation at the center and at the edges. However, nucleation from the corners remains the most likely. This nucleation from the corners can be explained by the fact that the SCO units located at the corners of the crystal relax the elastic stresses more easily on the surface because of their smaller number of neighbors.

F. Isothermal relaxation near the hysteresis loop

Here, we investigated the nonequilibrium properties of the system, at various temperatures ($T = 30, 45, 50$ and 54 K) near the thermal hysteresis loop of Fig. 7a using an elastic constant, $A_0 = 8000$ K.nm⁻². Interesting relaxation dynamics of metastable states are obtained according to values of model parameters. In experiments, after photo-irradiation to a long-lived HS state, by means of Light Induced Excited Spin State Trapping (LIESST) [26, 111–113], even that saturates HS fraction, n_{HS} , the relaxation process is visualized at low temperatures or by rapid quenching of the high temperature stable HS state. Using the same algorithm described in Sec. III, we performed the simulations starting from, a fully HS state, on a square lattice ($L = 32$), and used 25 independent runs. The obtained results are illustrated in Fig. 10, where the magnetization m , (panel a) and the HS fraction n_{HS} , (panel b) evolve according to the Monte-Carlo steps (MCS). Typical one-step relaxation curves are obtained and the behavior of m , and n_{HS} bear some resemblance. At low temperatures, from the hysteresis loop, sigmoidal curves are observed. From the outside to the interior of the loop, one remarks that the relaxation time increases when the temperature increases as reported in literature [50, 77, 79, 80]. This counter-intuitive behavior, where the relaxation

process of a metastable (or unstable) state slows down as the temperature increases, is due to the proximity of the lower branch of the thermal hysteresis, in which the HS state is thermodynamically stable, and so it has a long-lifetime.

In the next, Fig. 11 shows some transient states, taken also along the relaxation curves, at different simulation times, and temperatures $T = 50 K$ and $T = 54 K$. Horizontally, snapshots are obtained at the same coverage or concentration $n_{LS}(= 1 - n_{HS})$ of LS units excepted for panels $c(t_3)$ and $e(t_7)$. Vertically, they correspond to the same simulation temperature T . The same qualitative characteristics of clustering of LS domains were also observed in isothermal relaxation processes, from the metastable HS phase at the vicinity of the thermal hysteresis loop (see Fig. 11). On the other hand, all HS units have the same probability to switch, from HS state to LS state during HS \rightarrow LS transition, followed by volume decrease. Very close to the thermal hysteresis loop (see right panels of Fig. 11 where $T = 54 K$), one gets uniform aggregates of HS states, with some isolated LS units almost in their edges at the initial stage of the relaxation process. It is clear that, according to previous elastic model with open boundary conditions on 2D circular crystal, Nishino et al.[114] show that homogeneous macroscopic nucleation events occurred with long-range interactions for which single domain nucleation appears along the relaxation processes. As for the homogenous transformation of the magnetic system, while the magneto-elastic coupling contains both short and long-range effects, as we explained the long range effects of $J(r_{ij})$ depend on the quantity $\alpha(r_{ij} - R_{eq}^{HH})$ which is negligible in the HS region where the magnetic interactions are acting. Here, at different simulation times and fixed temperature, LS units are created and the domain growth is clearly observed from the corners as well as at the edges of the lattice configuration. Domain growth occurs in the diagonal directions, and a few one appears somewhere at the edges as previously observed in right panels of Fig. 9 (on cooling process). This happens by the way of the low cost energetic associated with the creation of an LS nucleus at the edges and mostly from the corners. These results are consistent and show good agreement.

V. CONCLUSION

Deformable lattice SCO model with ferromagnetic interactions is presented. It allows to reproduce thermal and spatio-temporal behaviors of SCO solids and Prussian Blue Analogs

(PBAs). The system of SCO compounds study is mapped on the Blume-Emery-Griffiths model with three-states ($S = \pm 1, 0$), where $S = \pm 1$ denote the magnetic HS state and $S = 0$ is associated to the diamagnetic LS state. These atoms interact elastically with their nn and nnn via anharmonic springs, whose elastic constants depend on their distances. Moreover, the nn sites also interact magnetically with an exchange interaction, whose value is a function of the instantaneous distance between the spin states. As a result, the magnetic interaction between the spin states depends on the elastic properties of the lattice. In the magnetic ordering, only HS atoms, with $S = \pm 1$ interact in the HS phase, while the spin-transition occurs between HS ($S = \pm 1$) and LS ($S = 0$) states. Finite-size effects have been detected at finite temperature on the model. This mapping allowed us to construct the phase diagrams of the model, from which gradual and first-order transitions are obtained, and on which the effects of the model interaction parameters are analyzed. The thermal dependence of the lattice configuration is studied upon heating and cooling along the thermal hysteresis loop with model parameters. This characterized the evolution of the system at a constant temperature, and revealed the mechanism of the nucleation and growth processes of the HS and LS phases as well as the organization of the magnetic state. The isothermal low temperature relaxation of the metastable HS states is also studied for which macroscopic nucleation phenomena was also identified. Compared to the previous elastic models, the present model has the advantage of producing a richer landscape of phase transitions according to the interaction between the magnetic, and the lattice subsystems. In particular, we found that the magnetic interaction act in an efficient way on the elastic properties of the lattice, by changing the thermal evolution of the average lattice bond-length in the HS state, while their effect is very limited on the HS fraction. All these results suggest that the electro-elastic models can be extended to investigate the problem of magneto-elastic interactions in PBAs and other related SCO materials with magnetic interactions. Extensions of this model considering antiferro-magnetic interactions instead of ferromagnetic ones, or other lattice topology leading to magnetic frustration might constitute an interesting extension of this work.

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Figure Captions

Figure 1: Lattice configuration showing the atomic links between a site i (red ball) connected to black and blue balls, representing the nn and nnn sites, respectively. The equilibrium bond-length between nn (nnn) SCO sites is $R_{eq}(S_i, S_j)$ ($R'_{eq}(S_i, S_j)$).

Figure 2: Thermal behavior of (a): HS fraction n_{HS} , (b): magnetization m , (c): magnetic susceptibility χ , and (d): average intermolecular distance $\langle d \rangle$ between nn SCO molecules, for four system sizes: 8×8 , 12×12 , 16×16 and 16×24 showing the finite-size effects on the model. Inset in panel (c) represents $\log(\chi_{max})$ as function of $\log(N^{-0.5})$ (black curve), and its corresponding linear regression (red curve). χ_{max} denotes the first peak height of χ , and N is the total number of SCO sites. Inset in panel (d) illustrates the correlation between n_{HS} and $\langle d \rangle$, for different system sizes considered, when temperature increases. The used parameters for all panels are: $A_0 = 2.10^3 \text{ K.nm}^{-2}$, $J_0 = 50 \text{ K}$, $\alpha = 100 \text{ K.nm}^{-1}$ and $\Delta = 450 \text{ K}$, and $g = 150$.

Figure 3: Some thermal behaviors of the model for 16×16 system and varying the values of the elastic constant A_0 with fixed other parameters. (a): HS fraction n_{HS} , (b): magnetization m , (c): magnetic susceptibility χ , and (d): average intermolecular distance $\langle d \rangle$ between nn SCO molecules. The curves show that one moves from a continuous behaviors to the appearance of discontinuities, which are first-order transitions, when A_0 increases. For large values of A_0 , the magnetic susceptibility χ , presents two peaks, where the first one corresponds to the first-order spin-transition, and the second one is attributed to the order-desorder transition. For all panels, other values of used parameters are: $J_0 = 50 \text{ K}$, $\alpha = 100 \text{ K.nm}^{-1}$, $\Delta = 450 \text{ K}$ and $g = 150$.

Figure 4: Some thermal behaviors of the model for 16×16 system and varying magnetic coupling interaction J_0 with fixed other parameters. (a): HS fraction n_{HS} , (b): magnetization m , (c): magnetic susceptibility χ , and (d): average intermolecular distance $\langle d \rangle$ between nn SCO molecules. Second- and first-order transitions are obtained for selected values of J_0 , and the curves shift to low temperatures by increasing J_0 values as obtained in our previous works [78, 79]. Two peaks appear in the magnetic susceptibility behavior at high values of J_0 , whereas only one depicted for its low values (see panel c). For all panels, other values of considered model parameters are: $A_0 = 10^3 \text{ K.nm}^{-2}$, $\alpha = 100 \text{ K.nm}^{-1}$, $\Delta = 450 \text{ K}$ and $g = 150$.

Figure 5: Some thermal behaviors of the model for 16×16 system and varying the magneto-elastic coupling α with fixed other parameters. (a): HS fraction n_{HS} , with inset that is the corresponding phase diagram, (b): magnetization m , (c): magnetic susceptibility χ , and (d): average intermolecular distance $\langle d \rangle$ between nn SCO molecules. Second- and first-order transitions are obtained, for selected values of α , and the curves shift to low temperatures by increasing α values. Two peaks appear in the magnetic susceptibility behaviors, at any values of α (see panel c). Dia-Ferro and Ferro-Para-magnetic phase transitions occurred as displayed the inset phase diagram in panel (a). For all panels, other values of considered model parameters are: $A_0 = 10^3 \text{ K.nm}^{-2}$, $J_0 = 60 \text{ K}$, $\Delta = 450 \text{ K}$ and $g = 150$.

Figure 6: Thermal phase diagram of the model in the reduced parameters $(A_0R_1^2/J_0, T/J_0)$, and $(J_0/A_0R_1^2, T/A_0R_1^2)$ planes for 16×16 system, with selected values of J_0 (panels a,b), and A_0 (panels c,d), respectively. Three phases are found: dia- para- and ferro-magnetic phases. Lines with solid circular dots (solid square dots) denote the equilibrium temperature $T_{1/2}$ (the first-order spin-transition temperature T_{fo} (first peak of χ)), whereas that with open circular dots are associated to order-desorder transition temperature T_C (second peak of χ). Large domain of ferromagnetic phase appears when the magnetic coupling interaction J_0 increases, and the phase diagram does not show tricritical points anywhere. Other model parameters values are: $\alpha = 100 \text{ K.nm}^{-1}$, $\Delta = 450 \text{ K}$ and $g = 150$.

Figure 7: Thermal hysteresis loop of the HS fraction, n_{HS} , at the vicinity of first-order transition for selected values of A_0 , and J_0 , respectively in panel (a) and (b). The system size is 32×32 . The loop area increases with the elastic constant A_0 , where their center is almost fixed in temperature. Whereas, for increasing J_0 values, the loop area increases and shifts to left for low temperatures. The inset in panel (b) shows thermal hysteresis loop of the magnetization m , for $J_0 = 100 \text{ K}$. $A, B, C, D, E, F, G,$ and H are the positions of lattice configurations of Fig. 9 on the upward, and backward branches, at different temperatures associated respectively to $T_1 = 26 \text{ K}$, $T_2 = 54 \text{ K}$, $T_3 = 74 \text{ K}$, $T_4 = 75 \text{ K}$, $T_5 = 76 \text{ K}$, $T_6 = 126 \text{ K}$, $T_7 = 56 \text{ K}$, and $T_8 = 55 \text{ K}$. We take $\Delta = 450 \text{ K}$ and $g = 150$ with other model parameters which are written in panels.

Figure 8: Phase diagram of 32×32 system, as function of $A_0R_1^2/J_0$, showing the dependence of limiting temperatures of hysteresis loops ($T_{1/2\uparrow}$, $T_{1/2\downarrow}$), and the associated equilib-

rium temperature approximated by $T_{1/2} = (T_{1/2\uparrow} + T_{1/2\downarrow}) / 2$ for $J_0 = 50 K$ (panel a) and $J_0 = 80 K$ (panel b). The corresponding hysteresis width ΔT are displayed in panel (c) and show increasing of loop area with $A_0 R_1^2$. Other values used for model parameters are: $\alpha = 100 K.nm^{-1}$, $\Delta = 450 K$ and $g = 150$.

Figure 9: Snapshots of lattice configuration for 32×32 system, along the thermal hysteresis loop of Fig. 7a, with $A_0 = 8.10^3 K.nm^{-2}$, during heating (left panels) and cooling (right panels) processes, at different temperatures $T_1 = 26 K$, $T_2 = 54 K$, $T_3 = 74 K$, $T_4 = 75 K$, $T_5 = 76 K$, $T_6 = 126 K$, $T_7 = 56 K$, and $T_8 = 55 K$. Green clusters are associated to those of LS units whereas, red (spin +1), and blue (spin -1) dots ones consist of HS unit clusters. It clear that the nucleation and growth process start from corners, and edges with deformations, and then propagated through the crystal. Values considered for other model parameters are: $J_0 = 50 K$, $\alpha = 100 K.nm^{-1}$, $\Delta = 450 K$ and $g = 150$.

Figure 10: Isothermal relaxation curves of 32×32 system, near the thermal hysteresis loop of Fig. 7a, for $A_0 = 8.10^3 K.nm^{-2}$, at different temperatures: $T = 30, 45, 50,$ and $54 K$. Relaxation time increases with temperature, and concave curves are got, from its initial stage. Red circular dots in panel (b) indicate the position, of spatio-temporal configurations in Fig 11, along the relaxation curves for $T = 50,$ and $54 K$. Other model parameters are the same in Fig. 7a with $A_0 = 8.10^3 K.nm^{-2}$.

Figure 11: Snapshots of lattice configuration, along the relaxation process for two temperatures, $T = 50 K$ (left panels), and $T = 54 K$ (right panels) at different simulation times: $t_1 = 27, t_2 = 496, t_3 = 1080, t_4 = 2980, t_5 = 52, t_6 = 1528, t_7 = 2386,$ and $t_8 = 8456 MCS$. Colors have the same meaning as in Fig. 9. Horizontal panels correspond to the same coverage n_{LS} of LS fraction, excepted for $c(t_3)$ and $e(t_7)$ configurations, while the configurations of vertical panels have been taken at the same temperature T . LS nuclei are formed from corners and edges, and grow to coalesce at high coverage. In (a), (b), (c), (d), and (e), respectively, 5, 23, 96, 99, and 53 percents of lattice are occupied by LS units. Values considered for other model parameters are: $A_0 = 8.10^3 K.nm^{-2}$, $J_0 = 50 K$,

$\alpha = 100 \text{ K.nm}^{-1}$, $\Delta = 450 \text{ K}$ and $g = 150$.

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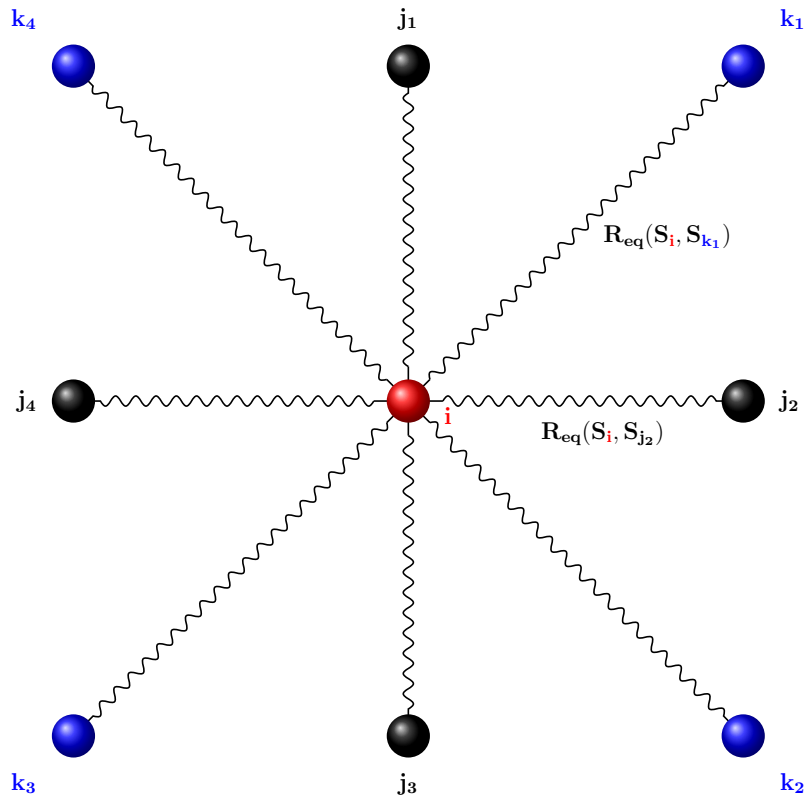


FIG. 1:

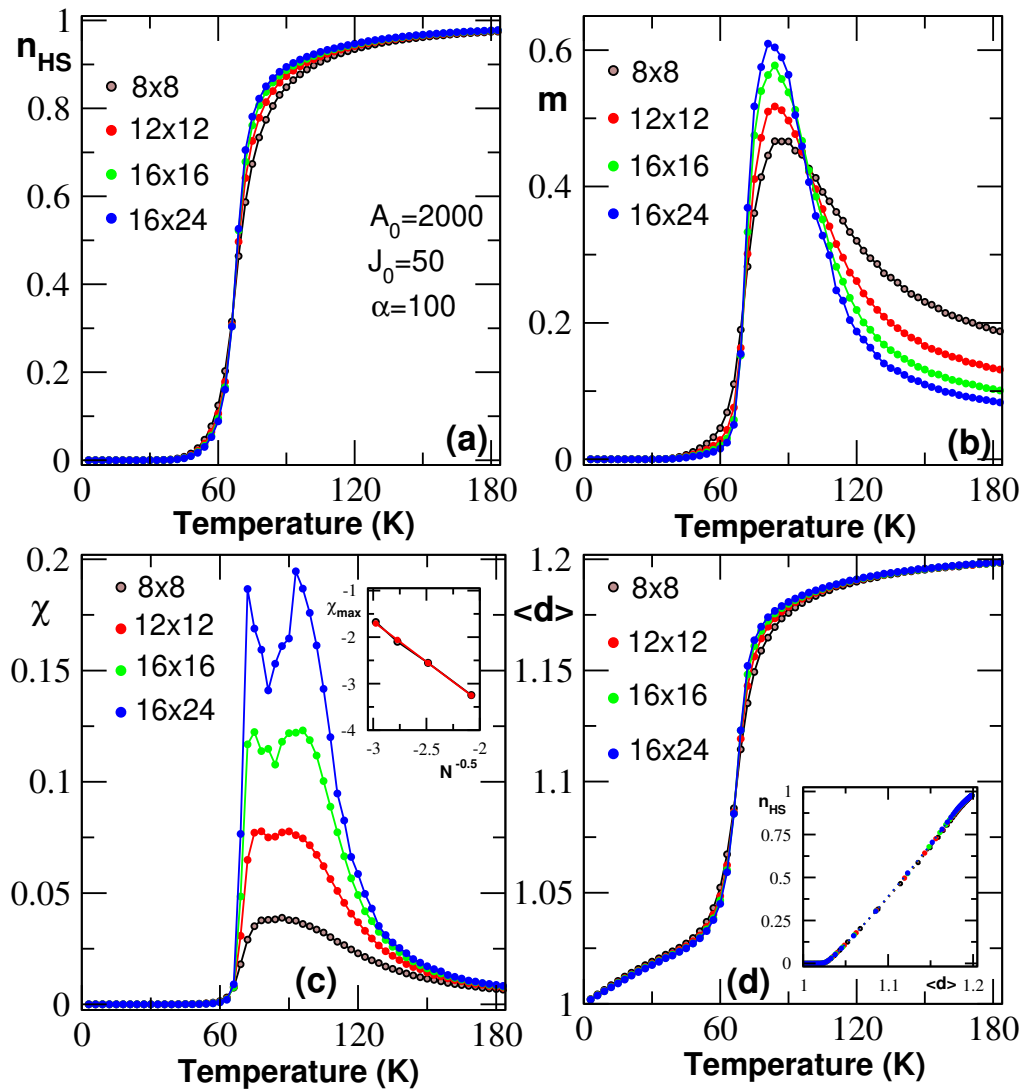


FIG. 2:

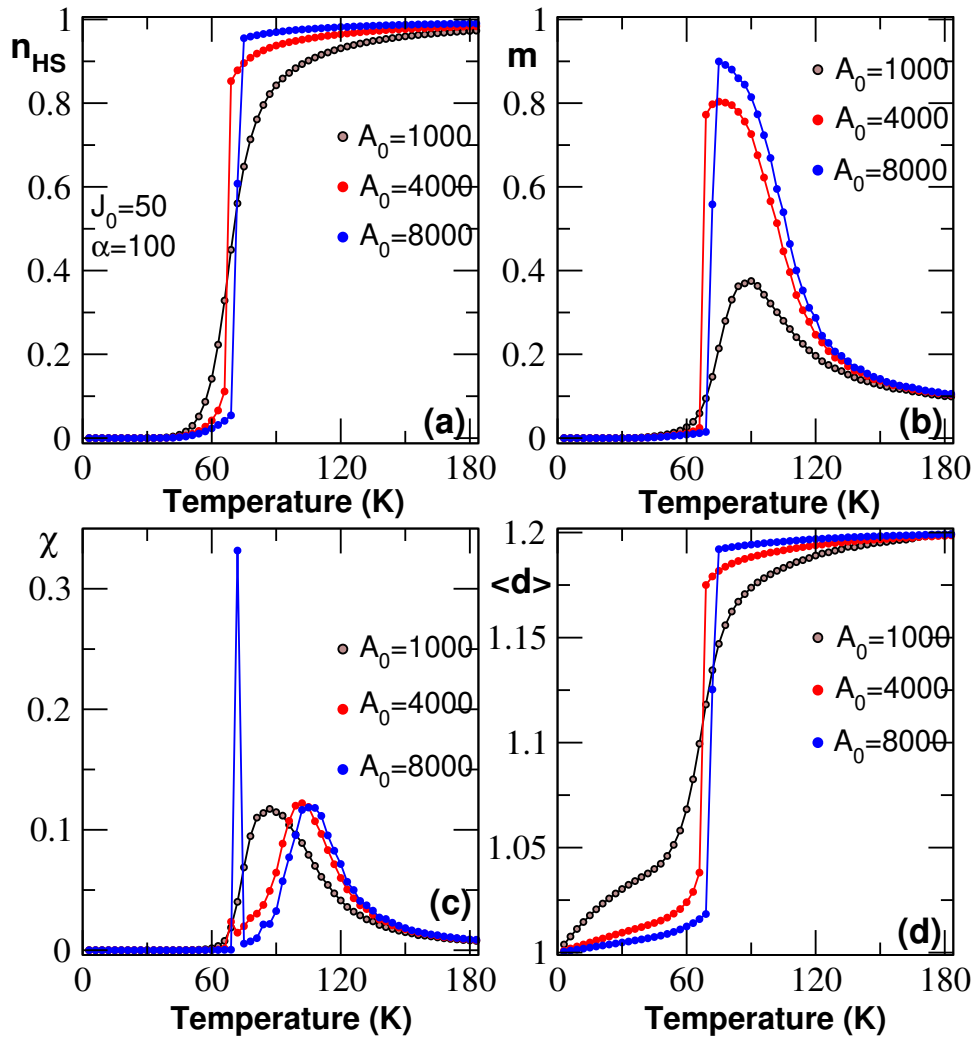


FIG. 3:

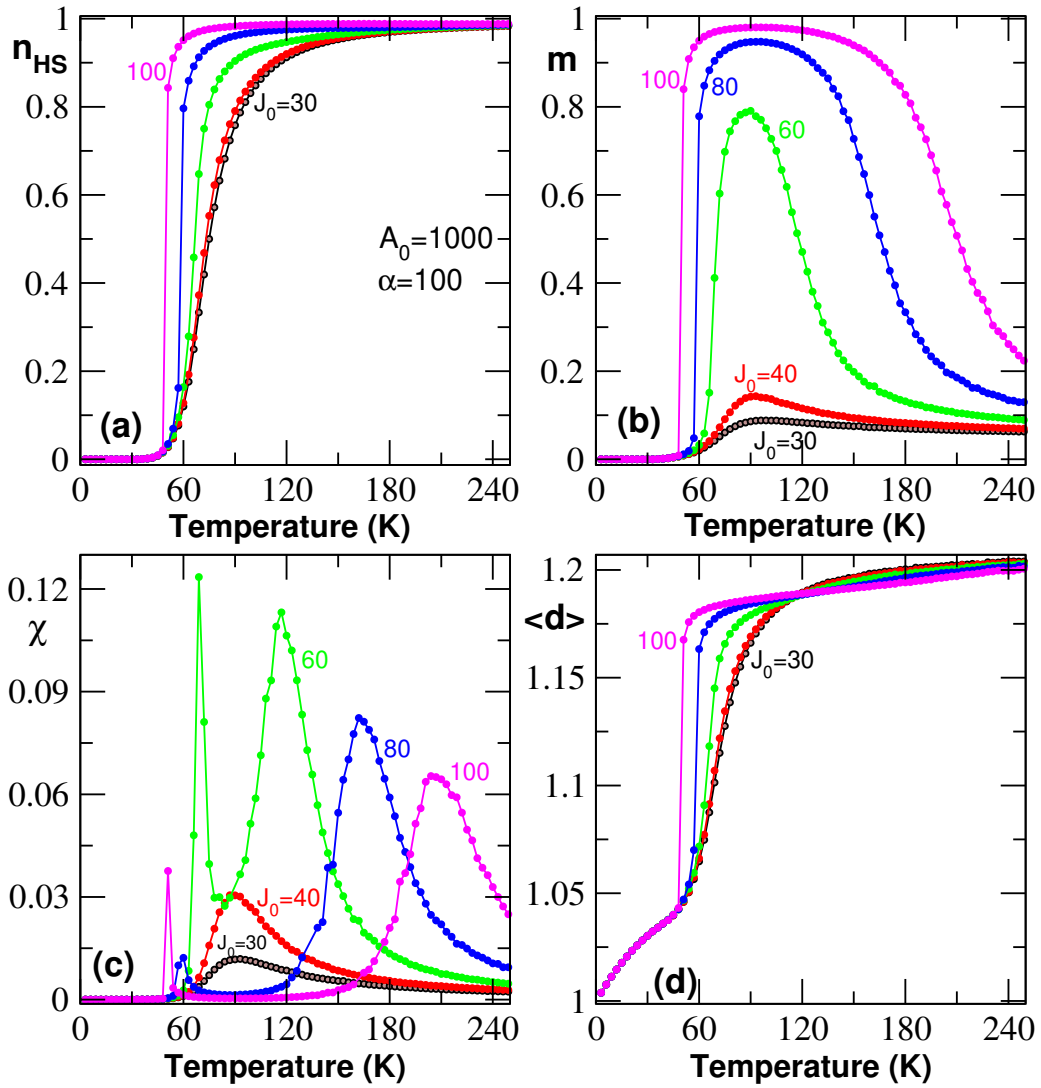


FIG. 4:

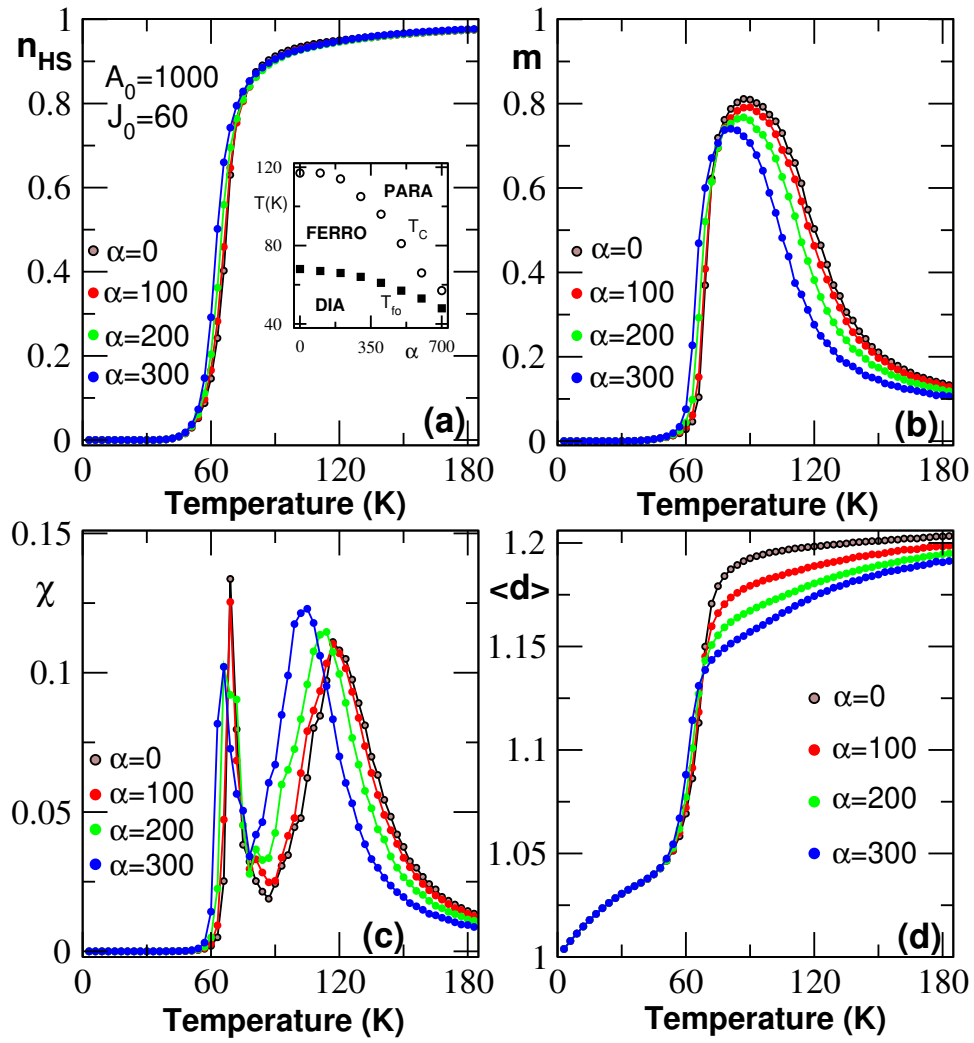


FIG. 5:

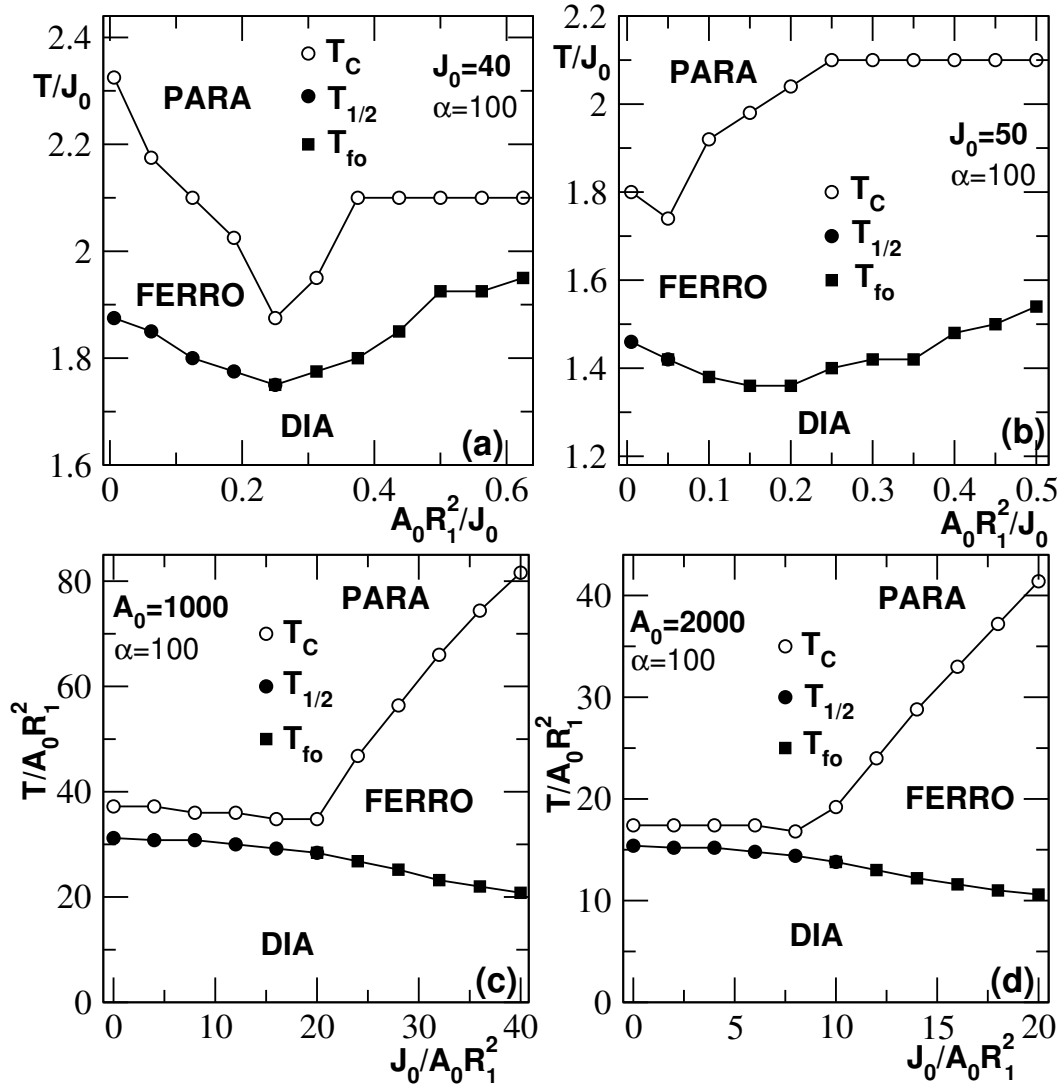


FIG. 6:

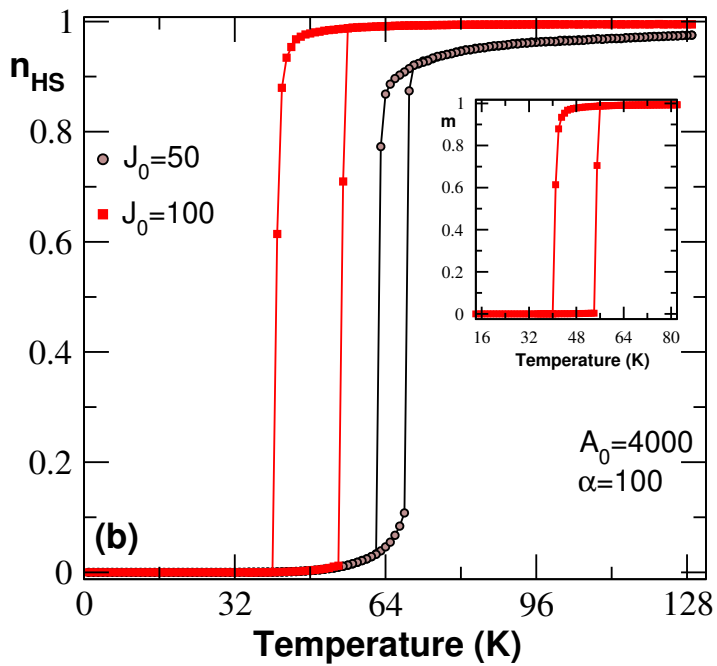
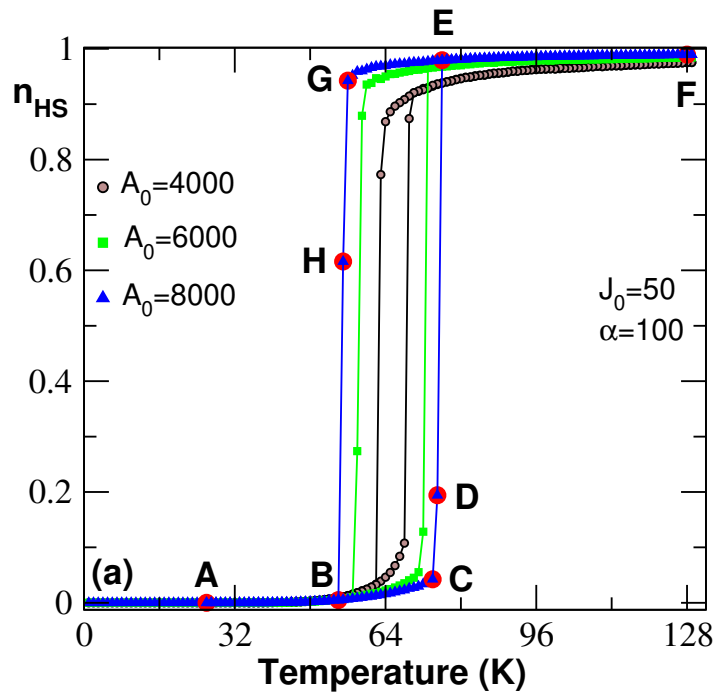


FIG. 7:

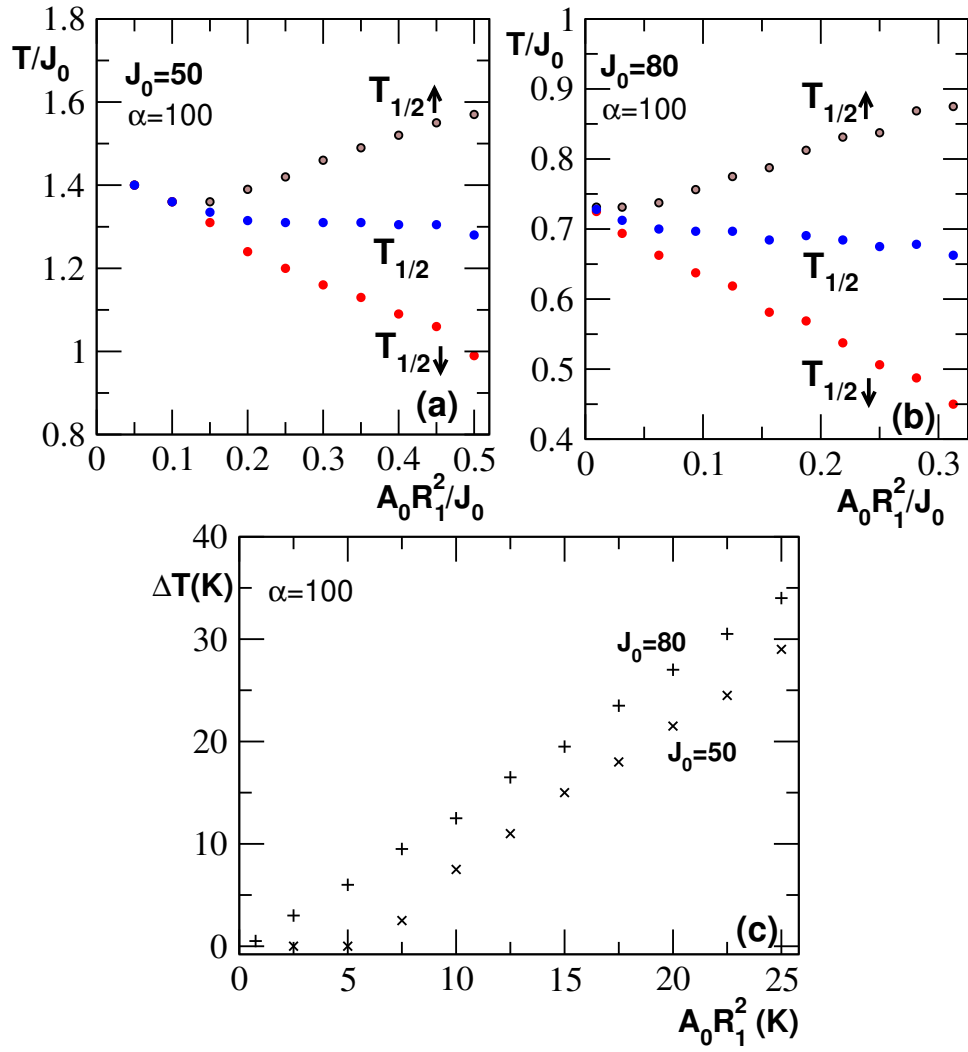


FIG. 8:

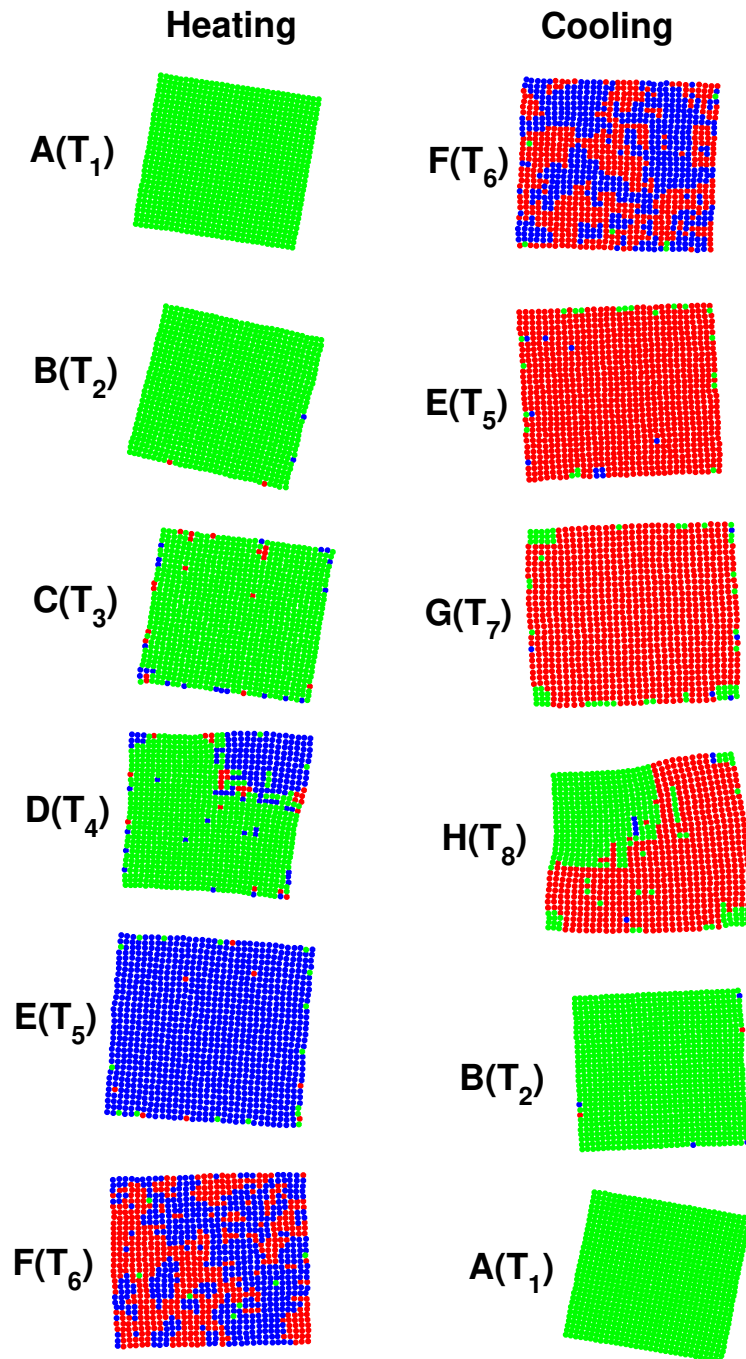


FIG. 9:

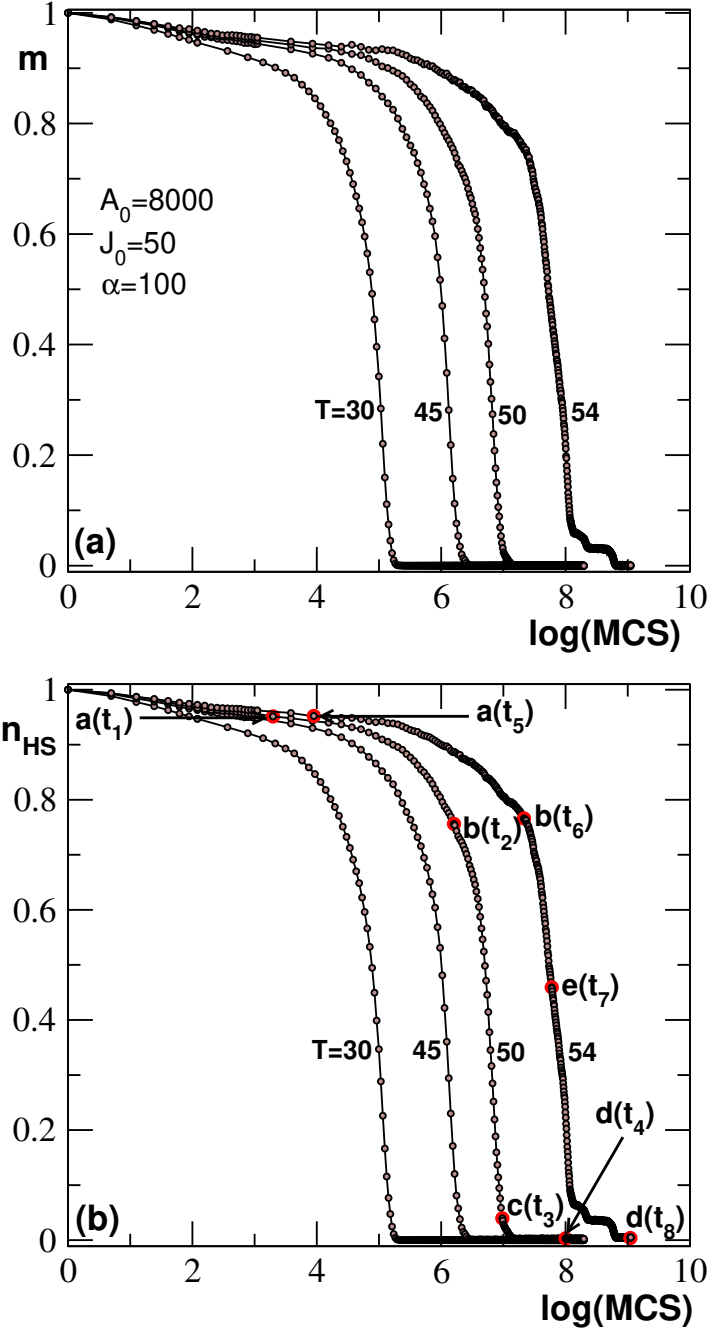


FIG. 10:

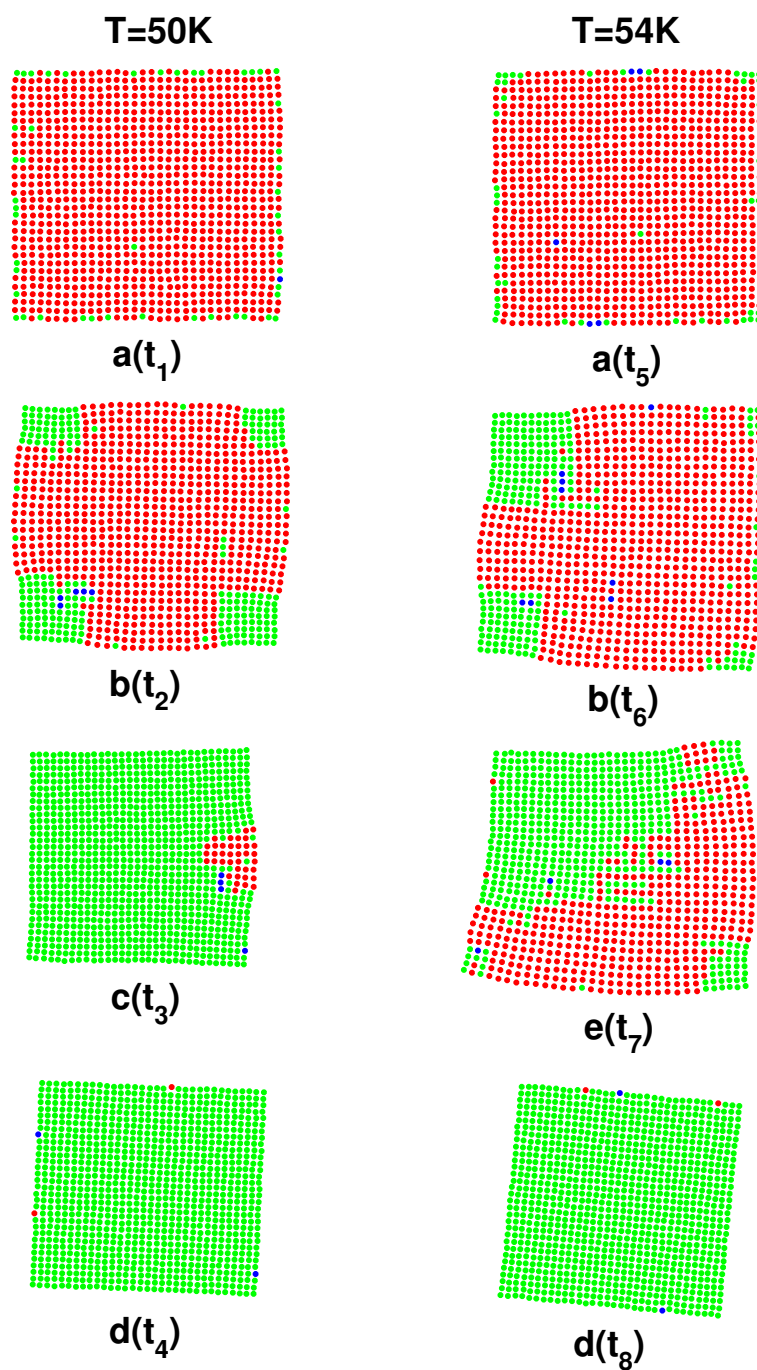


FIG. 11: