Monte Carlo simulation of bond-random spin-crossover compounds

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INTRODUCTION Spin-crossover (SCO) complexes are the transition metal coordination compounds with the electronic configuration ranging between $3d^4$ and $3d^7$ (manganese, iron, chromium, and cobalt) in (pseudo)octahedral surroundings. The variation of some external stimuli causes the reversible phase transition from low spin (LS) diamagnetic state to high spin (HS) paramagnetic state in SCO materials. There are the HS state with the electrons entering the d-orbitals as thermally accessible state and LS state with a maximum number of paired electrons in the $t2_g$ subshell as the electronic ground state.

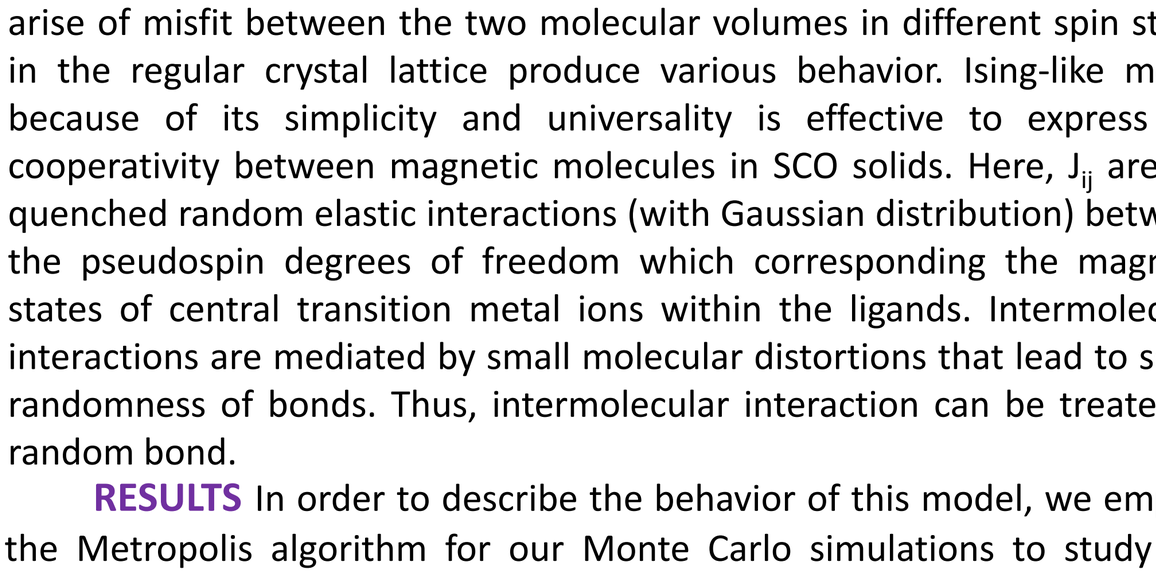
For the reason that the HS and LS states are characterized by different energies and degeneracies we employ the phenomenological microscopic Ising-like model for describing the behavior of spin-crossover regular crystals at molecular level where the two states are corresponding to HS and LS states respectively. The intermolecular interaction is contemplated in the nearest-neighbor limit with the following Hamiltonian

$$\mathcal{H} = -\frac{1}{2}\sum_{<i,j>} J_{ij} s_i s_j - h\sum_i s_i \qquad (1)$$

where < i, j > represents nearest neighbors of a lattice and s_i is the fictitious classical spin (pseudospin) for each site i (i = 1, 2, ..., N) with the eigenvalues ±1 that correspond to HS and LS states. For the simple two-dimensional model each spin is connected with z = 4 other spins on average chosen randomly. Next nearest neighbor contributions are not included. Periodic boundary conditions are applied.

The intermolecular interactions of elastic origin via a phenome-nological parameter accounting for the ferromagnetic coupling (J > 0) between magnetic centers i and j as two-level units are described by the first summand in the model (1). The intermolecular elastic interactions arise of misfit between the two molecular volumes in different spin states in the regular crystal lattice produce various behavior. Ising-like model because of its simplicity and universality is effective to express the cooperativity between magnetic molecules in SCO solids. Here, J_{ij} are the quenched random elastic interactions (with Gaussian distribution) between the pseudospin degrees of freedom which corresponding the magnetic states of central transition metal ions within the ligands. Intermolecular interactions are mediated by small molecular distortions that lead to some randomness of bonds. Thus, intermolecular interaction can be treated as random bond.

RESULTS In order to describe the behavior of this model, we employ the Metropolis algorithm for our Monte Carlo simulations to study the equilibrium properties of a 20 by 20 square Ising lattice using single spin-flips and periodic boundary conditions. Next nearest neighbor contri-butions are not included. For each data point, we take a measurement of every Monte Carlo trajectory for 10000 steps, after equilibrating for 1000 MC steps. In any event, each data point consists of 10000 MC attempts. For all parameters, we performed two separate calculations: heating and cooling.



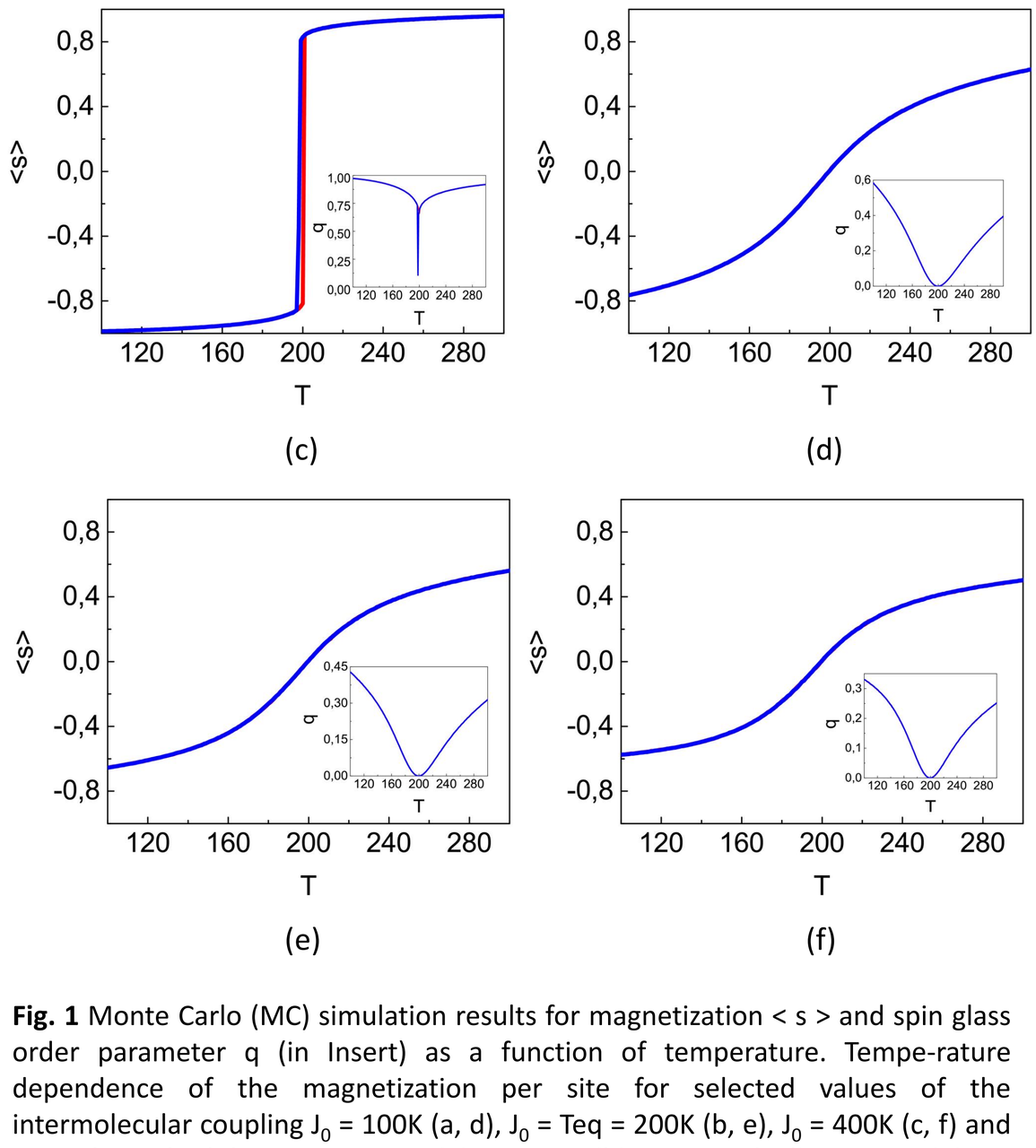


Fig. 1 Monte Carlo (MC) simulation results for magnetization < s > and spin glass order parameter q (in Insert) as a function of temperature. Tempe-rature dependence of the magnetization per site for selected values of the intermolecular coupling J_0 = 100K (a, d), J_0 = Teq = 200K (b, e), J_0 = 400K (c, f) and several standard deviation J = 50K (a), J = 100K (b), J = 200K (c,d), J = 400K (e), J = 800K (f) of intermolecular coupling. The other parameter values are Δ = 1000K and g = 150K.

The relationship of temperatures $T_c < T_{eq}$, $T_c = T_{eq}$ and $T_c > T_{eq}$ determines three characteristic types (gradual, sharp and hysteresis) of the behavior of spin-crossover systems. For an overall insight, six characteristic cases need to be researched for random bonds depended on the relation between the intermolecular coupling J_0 and the standard deviation J. The investigation results are summarized in **Fig. 1**. For better understanding of such regimes for different values of the deviation J, we have carried out series of numerical calculations of < s > and q for two opposite cases $J < J_0$ and $J > J_0$.

The hysteresis loops slow narrow up to vanishing as value J increases even the standard deviation J is small ($J < J_0 < kBT_{eq}$). Hysteresis loops are not framed for large values J as one can observe in Fig. 1. The system is undergoing in complete transitions for these cases. All the transitions are continuous. Magnetic order sets if $J_0 > J$.

SUMMARY

The Ising-like model of spin-crossover solid compounds with random bonds has been studied by intensive numerical Monte Carlo simulation. A numerical solution to the problem is found and analyzed.

Random distribution of intermolecular coupling results in the peculiarity of cooperative behavior, such as narrowing hysteresis loops or their vanishing or a more complex quasi-spin glass state. Our investigations could be helpful in the understanding of various patterns in real SCO systems.

The concept of spin-glass phase may be useful to understand of random bond spin-crossover compounds with share a very similar phenomenology to a spin glass.

REFERENCES

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