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ORIGINAL ARTICLE

Bond-random model of spin-crossover compounds: similarities and differences from spin glasses

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Abstract
The Ising-like model of spin-crossover solid compounds with random bonds has been studied by the mean-field (infinite range) replica symmetry approximation. An exact solution to the problem is found and analyzed. Interestingly, the temperature stability region at selected intermolecular couplings and standard deviations is quite wide.

Keywords Spin crossover · Bond random · Magnetization

Introduction

The transition metal coordination compounds with the electronic configuration ranging between $3d^4$ and $3d^7$ (chromium, manganese, iron, and cobalt) in octahedral surroundings, called spin-crossover (SCO) complexes, demonstrate reversible phase transition from a diamagnetic low spin (LS) to a paramagnetic high spin (HS) state upon variation of some external stimuli (temperature, pressure, light irradiation, magnetic and electrical fields) (Gütlich and Goodwin 2004; Halcrow 2013). In octahedral symmetry, only the HS and LS states are possible. For instance, the $3d^6$ complexes of ferrous ion have both ground state: with total spin number $S = 2$ (HS) and $S = 0$ (LS). The five d-orbitals of bivalent iron ion are split into three t_{2g}-(d_{xy}, d_{yz} and d_{xz} symmetries) and two e_g-orbitals (d_{z^2} and $d_{x^2-y^2}$ symmetries). The spin state is formed by the balance between the energy of orbital, needed to occupy all of the $3d$ levels (determined by the size of crystal field Δ), and the average energy of the Coulomb repulsion of the d-electrons. Due to interaction with crystal electric field, the ligand field splitting

$$\Delta = E(e_g) - E(t_{2g}), \tag{1}$$

that cause the spin pairing, fix the HS ground-state at low temperature. If the values of ligand field and Coulomb repulsions are approximately equal, the difference between the energy minima of the corresponding HS and LS terms will become comparable to the thermal energy. Under these conditions, both states are populated and the system is bistable. The SCO is one of the best examples of molecular electronic bistability. The possibility to address spin states through external stimuli opens the perspective of switches and magnetic storage (Kahn and Martinez 1998; Shepherd et al. 2013; Matsumoto et al. 2014; Mullaney et al. 2017; Kumar and Ruben 2017), environmentally friendly refrigerant materials (Gudyma et al. 2014b; von Ranke et al. 2018) and other nanoscale applications (Molnár et al. 2018; Salmon and Catala 2018; Kipgen et al. 2018; Takahashi et al. 2018; Boukheddaden et al. 2018) that gives the greatest promise.

Because of the HS and LS states have different energies and degeneracies, we use the microscopic Ising-like model for describing the behavior of spin-crossover regular crystals at molecular level. In this case, the intermolecular interaction is considered in the fully connected limit with the following Hamiltonian:

$$\mathcal{H} = -\frac{1}{2}\sum_{i\neq j} J_{ij} s_i s_j - h\sum_i s_i, \tag{2}$$

where s_i is the fictitious classical spin (pseudospin) for each site i ($i = 1, 2, \ldots, N$) with the eigenvalues ± 1 which correspond to HS and LS states, respectively. The first term in the model (2) describes the intermolecular interactions of elastic origin through a phenomenological parameter accounting for the ferromagnetic coupling ($J > 0$) between spins i and j as

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two-level units. In the regular crystal lattice, the intermolecular elastic interactions originating from misfit between the two molecular volumes in different spin states generate very rich behaviors. This is the simplest way to express the cooperativity between magnetic molecules in SCO solids (Gudyma et al. 2014a, 2015a, b; Rikvold et al. 2016; Chan et al. 2017). Here, J_{ij} are the infinite-range quenched random elastic interactions between the pseudospin degrees of freedom which represent the magnetic states of central transition metal ions within the ligands. In spin-crossover material, every site is in a specific local environment, generated by a ligand with particular features, and rather are not equivalent to each other. Randomness displays a disorder in local elastic forces between SCO molecules in different magnetic states. This lead to a "random-exchange" version of the Ising model. In a first approach, we merely take into account the existence of cooperativity without giving details of its origin. The random interactions J_{ij} are independently distributed according to Gaussian probability densities

$$P\left(J_{ij}\right) = (2\pi J^2/N)^{-1/2} \exp\left[-N(J_{ij} - J_0/N)^2/2J^2\right]. \quad (3)$$

The center of the distribution of randomness J_0 is essentially an intermolecular ferromagnetic coupling. The symbol J refers to the standard deviation of the distribution. Each spin interacts with all other spins. Thereat for all pairs of spins no matter how far they are apart

$$\begin{aligned} \left[J_{ij}\right]_{\mathrm{av}} &= J_0/N, \\ \left[J_{ij}^2\right]_{\mathrm{av}} - \left[J_{ij}\right]_{\mathrm{av}}^2 &= J^2/N, \end{aligned} \quad (4)$$

so that both J_0 and J are intensive quantities. The subscript *av* denotes an averaging over the J_{ij} distribution.

The second term characterizes the occurrence of intramolecular processes and describes the action of the crystal field on the spin-crossover site including the influence of the temperature:

$$h = -\frac{1}{2}\left(\Delta - k_{\mathrm{B}} T \ln g\right), \quad (5)$$

where Δ is the energy gap between HS and LS states of an isolated molecule; T is the absolute temperature; k_{B} is the Boltzmann constant; $g = g_{\mathrm{HS}}/g_{\mathrm{LS}}$ is relative degeneracy of SCO states. Due to both electronic and vibronic factors, the degeneracy of a HS excited state g_{HS} is necessarily larger than degeneracy of a LS ground one g_{LS}. The additional term of the ligand field proportional to heat energy $k_{\mathrm{B}}T$ is justified by the internal entropy effects. According to their nature, the physical meaning of h is the Gibbs energy difference per molecule between the fully HS and LS crystals, i.e., the chemical potential difference of HS and LS species. Note that Hamiltonian (2) was hereinafter used à la the Sherrington–Kirkpatrick model based on the spin mean field theory, where all points are connected and the limit of infinite dimensions is applied. This makes it possible to accurately solve the proposed model. To take into account the real dimension of the system, as a rule, numerical Monte Carlo modeling is used.

In a previous paper by one of the authors (Gudyma et al. 2020), a theoretical approach to SCO molecular crystals was examined, where a simple the Ising-like model of spin-crossover solids with quenched random ligand field was considered by the mean-field (infinite-range) approximation. In this paper, we aim to present exact solution of Ising-like model of spin-crossover solid compounds with a Gaussian-distributed random intermolecular coupling, by means of the replica method. In the next section, we start by analyzing the model and discussing its replica-symmetric solution. In "Phase diagram and magnetization. Results and discussion", we present our calculations and the resulting magnetic phase diagram. Finally, we synopsize our findings in the last section.

The model with a Gaussian-distributed random intermolecular coupling

For the vanishing of the variance J^2, the Hamiltonian (2) is adapted from the Wajnflasz–Pick model for the Ising-like two-level interacting systems, describing the main aspects of cooperative behavior of spin-crossover materials (Wajnflasz and Pick 1971). The model, successfully used for reproducing various aspects of the ordering processes in spin-crossover compounds, reflects the molecular origin of the spin-crossover phenomenon, and its dependence on intermolecular interactions (Bousseksou et al. 1992; Boukheddaden et al. 2000; Muraoka et al. 2011; Chiruta et al. 2012; Paez-Espejo et al. 2014; Watanabe et al. 2016; Rikvold et al. 2016). The microscopical Hamiltonian of model (2) may be considered as phenomenological and reproduces fairly well experimental transition curves. As mentioned in the microreview (Pavlik and Boča 2013), the characteristic features of the Ising-like model (2) and (5) include wide abstraction and generality, providing suitable standards referred as starting points by other new and more refined approaches (Enachescu et al. 2012; Slimani et al. 2013; Nishino et al. 2013; Bertoni et al. 2016; Gueddida and Alouani 2016; Enachescu et al. 2016).

The most commonly as a natural order parameter in this problem, the HS fraction is used. It (the mean number of molecules in the HS state) is defined as

$$n_{\mathrm{HS}} = (1 + < s >)/2, \quad (6)$$

where the average fictitious spin or the fictitious magnetization is

$$< s >= \frac{1}{N}\sum_i s_i. \tag{7}$$

We will use the last quantity as an order parameter. One of the advantages of this choice is connected with the fact that the external field is coupled linearly to this order parameter. In the noninteracting system, the equilibrium temperature T_{eq}, at which HS fraction and LS fraction is equal, corresponds to a zero effective field h. It is related to the energy gap and the entropic energy as follows $T_{eq} = \Delta/k_B \ln g$. And conversely, the critical temperature T_c, at which the phase transition happens in standard ferromagnetic Ising systems, depends only on the interaction parameter J_0, which appears in Hamiltonian (2). If the critical temperature T_c is smaller than the equilibrium temperature in noninteracting model, then a gradual spin transition (supercritical crossover) from LS to HS takes place by increasing the temperature. Otherwise, the spin transition is discontinuous and is associated with the first-order phase transition. In this case, such systems evolve following a path of metastable states and exhibit hysteresis due to the existence of energy barriers larger than thermal fluctuations. In contrast to the equilibrium temperature T_{eq}, the critical temperature depends on the interaction parameter J_0, inasmuch as in the mean-field approximation $T_c = 2J_0/k_B N$. In thermodynamic approach, it vanishes and the phase transition at finite temperature becomes impossible.

Phenomenologically at microscopic level, an individual spin-crossover molecule is regarded as an isolated bistable unit. The interaction with the surroundings basically modulates the zero-point energy difference of the individual molecule and the change of the spin state—SCO phenomenon—may occur at microscopic scale due to the coupling between the electronic and vibrational structures of the molecules (Kambara 1981). In the zero-order mean field approximation, the external field h is regarded as identical for all molecules in the sample and for all times, and represents the average coordination environment of the transition metal ion sites.

It is always of interest when a mathematical model of a physical system turns out to be exactly solvable even when realistic approximations have to be made. Here we would like to describe such a model and to study its behavior, particularly at the line of transitions. As was discussed earlier, the responsible factor driving the cooperativity is the long-range elastic interaction arising due to interaction between local lattice distortions at each molecular unit, because of the size difference between the HS and LS molecules. A HS → LS transition is accompanied by a significant structural change involving a compression in the metal-donor atom distance. In the presence of random distribution HS and LS states on neighboring sites, the local interactions are disorder. At local quenched and time-invariant disorder, the intermolecular interactions are distributed according to Eq. (3). A novel feature of these systems compared to standard Ising-like theory of spin-crossover compounds consists in the fact that substitutional disorder generates local quenched random couplings. This circumstance plays an important role since it defines the random-bond Ising model with a uniform field (Kirkpatrick and Sherrington 1978; Binder and Young 1986) and it allows us to formulate the problem of SCO solids in terms of theory of spin glasses in a random uniform magnetic field.

Frustration and quenched randomness are two important ingredients in Ising spin glass problems. To obtain the thermodynamic properties of the system, one must first calculate all thermodynamic quantities for a given random distribution of intermolecular couplings and then average the results with the distribution $P(J_{ij})$. The Helmholtz free energy of the system averaged over this probability distribution can be obtained via the well-known replica trick formalism for the partition function Z. We use the replica trick to re-express the free energy in terms of the moments of Z:

$$\langle F\rangle_{av} = -k_B T \frac{\partial}{\partial n}|_{n=0} \langle Z^n\rangle_{av}\,. \tag{8}$$

We recall that the brackets < ... > mean the thermal expectation value, with the subscript av signifying an average over the intermolecular couplings (the configurational average). In the thermodynamic limit the replica-symmetric solution for the disorder-averaged free energy per spin is

$$\begin{aligned} -\beta f =& \frac{(\beta J)^2}{4}(1-q)^2 - \frac{\beta J_0}{2}m^2 \\ &+ \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} e^{-z^2/2}\ln\left[2\cosh(\beta H(z))\right]\mathrm{d}z, \end{aligned} \tag{9}$$

where the typical magnetization m is fixed through the implicit (self-consistent) equation

$$m = \langle\langle s_i\rangle\rangle_{av} = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty} e^{-z^2/2}\tanh(\beta H(z))\mathrm{d}z, \tag{10}$$

with $\beta = 1/k_B T$. Here, the internal angular brackets denote conventional thermal averaging, with all h_i's given. Schneider and Pytte showed that the replica technique ensures the exact result for the random-field Ising model, i.e. the model is solved exactly.

To discuss the thermodynamic properties of this model, we introduce also the independent spin-order parameter or Edwards–Anderson spin-glass order parameter Edwards and Anderson (1975) as follows:

$$q = \left\langle \langle s_i \rangle^2 \right\rangle_{\mathrm{av}} = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{-z^2/2} \tanh^2(\beta H(z)) \mathrm{d}z. \quad (11)$$

In contrast to the magnetization m that characterize a pure-state of a quasi spin-glass, this parameter is an overlap of two pure states. It was also to be observed that nonzero q indicates the existence of magnetic moments, while $m \neq 0$ in addition to $q \neq 0$ indicates that the moments are ferromagnetically ordered. Here $H(z)$ related to m and q by

$$H(z) = Jq^{1/2}z + J_0 m + h. \quad (12)$$

From (10) and (11), we see that $H(z)$ can be interpreted as the local molecular field acting on a site. Different sites have different fields because of disorder, and the distribution is Gaussian with mean $J_0 m + h$ and variance $J^2 q$.

Phase diagram and magnetization. Results and discussion

Real properties of spin-crossover compounds differ significantly from classic Ising spin glass. The case of spin-crossover molecules is more complex. Due to degeneracy of states, the total Ising magnetic field is nonzero in our model and breaks the original Z_2 symmetry under $s_i \to -s_i$ and thus destroys the Ising critical point. For Ising spin glass, it is possible to obtain analytical results in limiting cases for $J_0 = 0$, $\Delta \to 0$ or $T \to 0$ that are unrealistic for real spin-crossover system. On the other hand, the self-consistent mean-field equations can be solved numerically for a given J_0, J and Δ versus temperature T by an iterative method.

As we have already pointed out in "Introduction", there are three characteristic types of the temperature behavior of spin-crossover materials determined by the relationship of temperatures $T_c < T_{eq}$, $T_c = T_{eq}$ and $T_c > T_{eq}$. They are shown in Fig. 1 for the case of absence random distribution of bonds ($J = 0$).

Consequently, six characteristic cases need to be researched for random bonds are depending on the relation between J_0 and J. To better appreciate such regimes for different values of the deviation J, we have carried out series of numerical calculations of m and q for two opposite cases $J < J_0$ and $J > J_0$ (see, Fig. 2).

One can see that the occurrence of a smooth or sudden variation m and q are strongly dependent on the used values of intermolecular coupling parameters J_0. A random distribution of intermolecular bonds destroys the magnetic order in the system. The hysteresis loops slow narrow up to vanishing as value J increases even the standard deviation J is small ($J < J_0 < k_B T_{eq}$). As illustrated graphically in Fig. 2, no hysteresis loops are formed for large values J. If $J_0 > J$, magnetic order sets and reached phase is ferromagnetic, and when the converse is true, quasispin-glass order results, and m is keeping zero for $k_B T \ll J$. Indeed the spin-glass order parameter q values are seen to increase with decreasing temperature to zero. However, due to the fact that the competition between the actions of standard deviation of random bonds J and the "magnetic field" h (5), the spin-glass order parameter q can also increase for high temperatures (in this case, the magnetization per spin m is also not equal to zero).

In Fig. 3, we show the disorder-averaged free energy spin per spin f vs temperature T at selected values J_0 and J.

Inasmuch as the free energy f shows a maximum the entropy $S(\equiv -\partial f/\partial T)$ has negative values in the low-temperature region. The third law of thermodynamics according to which such concepts as de Almeida–Thoules (AT) stability condition and replica symmetry breaking have been introduced in spin-glass theories is violated by this fact. We should investigate whether the replica-symmetric solution of the bond-random spin-crossover model is

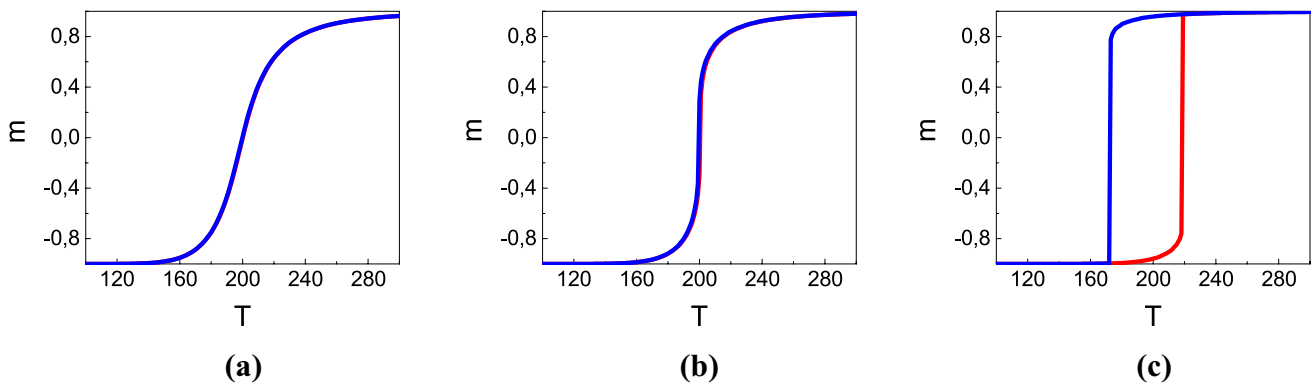

Fig. 1 Characteristic (gradual, sharp and hysteresis) types of the temperature behavior of magnetization in spin-crossover materials. Temperature dependence of the magnetization per site for selected values of the intermolecular coupling $J_0 = 100$ K (**a**), $J_0 = T_{eq} = 200$ K (**b**), $J_0 = 400$ K (**c**). The other parameter values are $\Delta = 1000$ K and $g = 150$ K

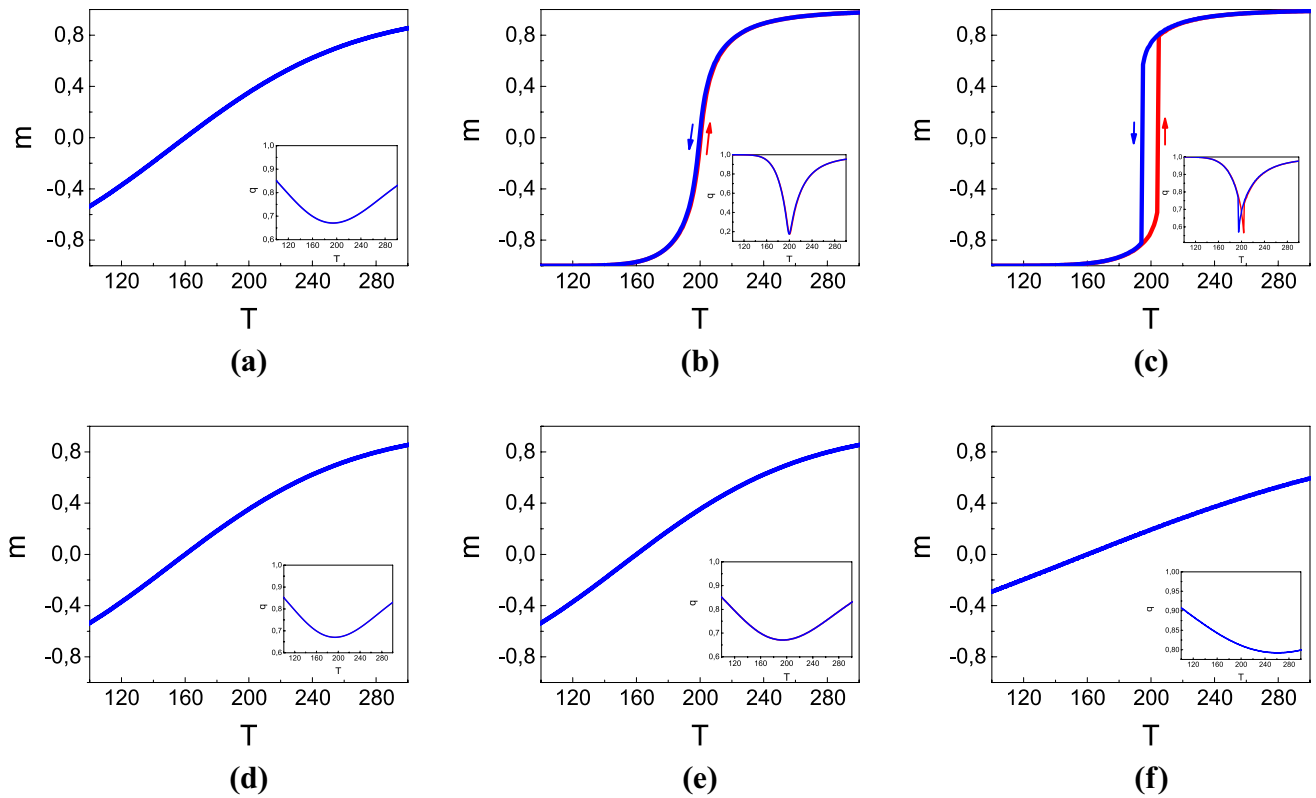

Fig. 2 Examples of magnetization m and spin glass order parameter q (in Insert) as a function of temperature. Temperature dependence of the magnetization per site for selected values of the intermolecular coupling $J_0 = 100$K (**a**, **d**), $J_0 = T_{eq} = 200$ K (**b**, **e**), $J_0 = 400$ K (**c**, **f**) and several standard deviation $J = 50$ K (**a**), $J = 100$ K (**b**), $J = 200$ K (**c**, **d**), $J = 400$ K (**e**), $J = 800$ K (**f**) of intermolecular coupling. The other parameter values are $\Delta = 1000$ K and $g = 150$ K

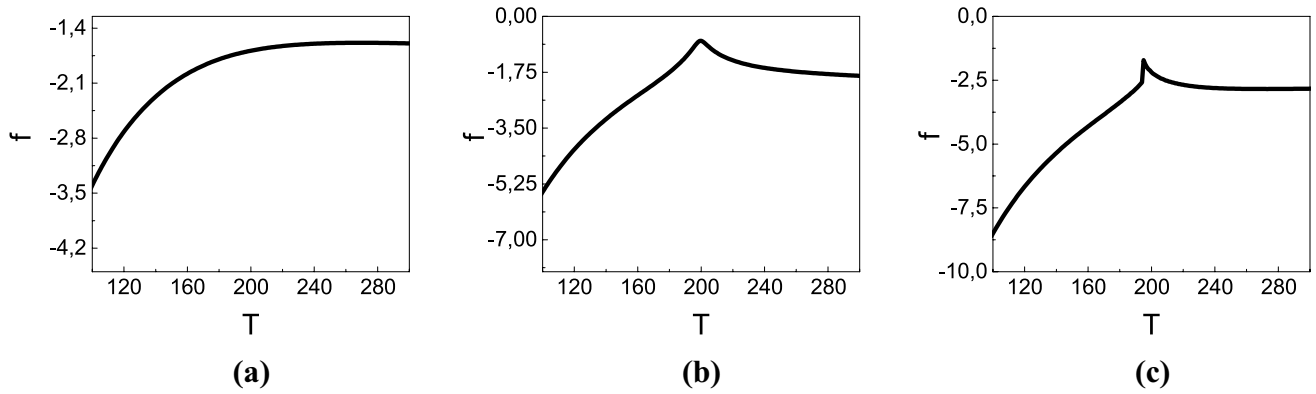

Fig. 3 Free energy f vs temperature T for spin-crossover materials. Temperature dependence of the magnetization per site for selected values of the intermolecular coupling and standard deviation $J_0 = 100$ K, $J = 50$ K (**a**), $J_0 = T_{eq} = 200$ K, $J = 100$ K (**b**), $J_0 = 400$ K, $J = 200$K (**c**). The other parameter values are $\Delta = 1000$ K and $g = 150$ K

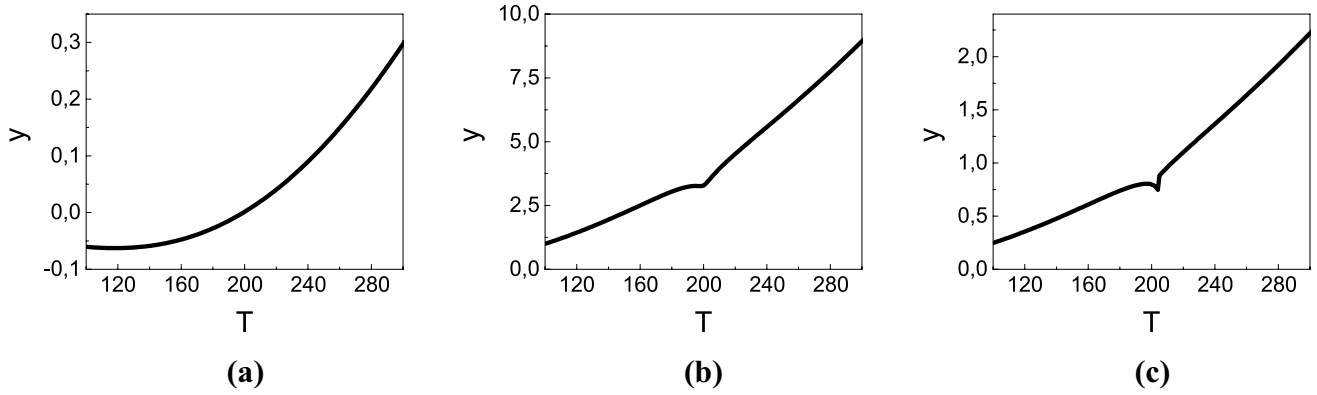

Fig. 4 Function y vs temperature T for selected values of the intermolecular coupling and standard deviation $J_0 = 100$ K, $J = 50$ K (**a**), $J_0 = T_{eq} = 200$ K, $J = 100$ K (**b**), $J_0 = 400$ K, $J = 200$ K (**c**). The other parameter values are $\Delta = 1000$ K and $g = 150$ K

unstable in the whole spin-glass phase or not. As is known, de Almeida–Thouless stability condition of replica-symmetric solution under the static approximation is given by

$$y = \left(\frac{T}{J}\right)^2 - \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} e^{-z^2/2} \operatorname{sech}^4\left(\frac{H(z)}{T}\right) \mathrm{d}z \geq 0. \quad (13)$$

In Fig. 4, we display the temperature dependence of AT stability region at selected intermolecular couplings and standard deviations.

For small values J_0 and J the AT line of Eq. (13) locates the stability limit at T_{eq}. But the AT line extends the stable region to zero temperature when $J_0 \geq T_{eq}$.

Concluding remarks

Apparently, spin-crossover compounds with random intermolecular coupling have widely occurred among molecular crystals. The provided model of infinite size and dimensionality for spin-crossover crystals has the exact solution given by the mean field approximation. The replica-symmetric solution discussed in this paper corresponds to a quasi-equilibrium metastable state of the system, in close analogy to the SK theory for magnetic spin glasses. For strong intermolecular interactions, the replica-symmetric assumption is performed for wide temperature interval. In the paper, six characteristic cases of temperature behavior of spin-crossover compounds for random intermolecular bonds have researched.

Degenerate energy levels of molecular core determine the fundamental behavior of spin-crossover compounds such as the presence and location of equilibrium temperature T_{eq}. The intermolecular coupling leads to cooperativity in spin-crossover system and as a consequence to phase transition. Random distribution of intermolecular coupling results in peculiarity of cooperative behavior, such as narrowing hysteresis loops or their vanishing or a more complex quasi-spin glass state. The successful implementation of described approach for providing a facile way to include random intermolecular interactions paves the way for future research about the role of such interactions within SCO compounds.

Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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