

Richness of the nature of intermolecular interactions in spin-crossover materials and its implications

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Thermally induced spin transition materials are known for their potential applications in a wide range of fields, from pressure and strain sensing to high-density information storage and control. The latter are described by Ising-like models and elaborate elastic theories including the coupling between the change of spin state and the accompanying local deformation of the lattice during the transition. In the present work, the Morse potential is used to model interactions between spin-transition molecules. The resultant Hamiltonian is solved by searching first for the mechanical equilibrium, revealing an isomorphism with an Ising-like model, including competing short- and long-range interactions with the presence of anharmonic effects. Studies within the molecular field approximation, Bethe-Peierls, and Monte Carlo methods allow reproducing several experimental situations among which gradual, first-order, and two-step transitions are observed, demonstrating the ability of the model to capture the diversity of spin-crossover materials while comparing the different methods and their limitations.

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I. INTRODUCTION

First-row transition metal ions demonstrate the capacity to adopt diverse spin states in response to external ligand fields, a property crucial to their physical and chemical functionality. A significant manifestation of this spin-state variability is the phenomenon of spin crossover (SCO), wherein molecular or framework compounds transition between high-spin and low-spin states under external physical influences. Notably, structural transformations associated with spin crossover influence the electronic configuration of magnetic centers, thereby modulating their magnetic properties. The electronic phenomenon of spin crossover has a strong connection to the crystal lattice. Therefore, SCO compounds of $3d^4$ – $3d^7$ metal ions, which demonstrate reversible transitions between high-spin (HS) and low-spin (LS) states in reaction to external stimuli, are also affected by structural alterations in the coordination geometry of the metal centers. Spin-crossover metal complexes represent a quintessential class of magnetic molecular materials, distinguished by their ability to switch behavior and asymmetric bistability at the molecular level. Molecular electronics, high-density magnetic data storage, display technologies, and dye-sensitized solar cells are just a few of the areas where transition-metal complexes hold great promise for future applications [1–5].

In bulk systems, SCO molecules frequently display cooperative behavior during spin-state transitions, primarily due to elastic interactions stemming from volume disparities between high-spin (HS) and low-spin (LS) states. The degree of these cooperative effects is typically inferred from the steepness of the spin-transition curve as a function of temperature. When spin-state interactions promote pairings of identical configurations (HS–HS or LS–LS), the behavior is classified as cooperative, similar to ferromagnetism, whereas interactions favoring alternating spin states (HS–LS) are considered antiferromagnetic, akin to antiferromagnetic interactions. Understanding the conditions that enhance cooperativity in SCO systems is crucial to optimizing their practical applications. Most SCO systems are based on pseudo-octahedral iron(II) complexes with electronic configuration $3d^6$ and nitrogen-donor coordination environments. These ligands establish a ligand field-splitting energy comparable to that of the spin-pairing energy. At low temperatures, the ground state for these molecules is represented by the low-spin electron configuration ($t_{2g}^6 e_g^0$) with $S = 0$. However, entropic contributions to the Gibbs free energy associated with spin degrees of freedom cause the high-spin electron configuration ($t_{2g}^4 e_g^2$) with $S = 2$ to become significantly thermally populated at high temperatures. An important characteristic of the SCO phenomenon is the interplay between short- and long-range lattice interactions, which collectively facilitate solid-state cooperativity. Experimental observations, such as hysteretic and multisteped spin transitions, provide evidence for these interactions [6–13]. Additionally, elastic frustration plays a critical role in inducing multistep transitions, which result from competing ferroelastic-like and antiferroelastic-like interactions. In most cases, cooperativity in SCO systems adheres to mean-field approximations and does not extend beyond the Weiss molecular field or Bragg-Williams approximations.

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We initially demonstrate the primary mechanism by introducing a basic model for the elastic interaction of spin-crossover molecules, based on the Morse potential [14]. We demonstrate that structural transformations significantly impact the electronic configuration of magnetic centers, ultimately facilitating switchable magnetic properties. The goal of this paper is to explain how structural changes in materials lead to the richness of their magnetic behavior, with potential implications for material design and application.

II. MODEL HAMILTONIAN

In this paper, we adopted the static Ising-like model previously developed to describe the equilibrium properties of SCO solids [15]. The proposed model characterizes the SCO in terms of a binary-state fictitious spin description, where s_i is a fictitious spin that has two eigenvalues $s_i = +1$ and $s_i = -1$, which are, respectively, associated with the HS and LS states of the molecule. The fictitious spins (denoted s) represent the two possible electronic states of the spin crossover molecule with different degeneracies of the two spin levels. The intermolecular pairwise interaction in an SCO molecular crystal is approximated by the Morse potential energy. The choice of the potential is due to the fact that in the mean-field theory, denominators dependent on the spin state of molecules do not arise for it, in contrast to the approach presented in Ref. [15] (see the Appendix). We presume that the intermolecular interactions are bimolecular and occur only between the nearest-neighboring sites. Accordingly, the total energy of the system in a lattice of N spin-active centers, each molecule pairwise interacting with z nearest neighbors, is given by the Hamiltonian

$$\mathcal{H} = \epsilon \sum_{(ij)} (1 - \exp(-b(r_{ij} - a_{ij})))^2 - h \sum_i s_i. \quad (1)$$

In this context, ϵ represents the depth of the potential well, while r_{ij} denotes the distance between the metal centers i and j of two interacting molecules. The effective parameter b governs the width of the potential, so that the quantity $\epsilon \times b^2$ is equivalent to an elastic constant. The value a_{ij} corresponds to the distance at which the intermolecular potential between the two particles becomes minimum, commonly referred to as the equilibrium bond length between the sites i and j , carrying the spin states s_i and s_j . This length is expressed as a function of s_i and s_j in the following manner

$$a_{ij} = a_{\text{HL}} + \frac{\delta a}{4}(s_i + s_j), \quad (2)$$

where $\delta a = a_{\text{HH}} - a_{\text{LL}}$ is the lattice parameter misfit between the HS and LS states and $a_{\text{HL}} = \frac{a_{\text{HH}} + a_{\text{LL}}}{2}$. Consequently, the interactions between molecules in the LS-LS, LS-HS, and HS-HS pairs exhibit variances. It follows that the potential energy curves demonstrate different minima for different electronic states. The Morse potentials as a function of the distance between the metal centers of two interacting molecules for the three cases HS-HS, HS-LS, and LS-LS are shown in Fig. 6 in the Appendix.

The second term in the Hamiltonian (1) is an intramolecular contribution that accounts for the influence of the crystal field on the spin-crossover site, incorporating temperature

dependence due to entropic effects. The expression of the effective ligand field h is

$$h = -(\Delta - k_B T \ln g), \quad (3)$$

where 2Δ is the energy gap between HS and LS states of an isolated molecule; T is the absolute temperature; k_B is the Boltzmann constant; $g = (g_{\text{HS}}/g_{\text{LS}})^{1/2}$ is the relative degeneracy of SCO states. The different energy and degeneracies of the HS and LS states are taken into account as an effective temperature-dependent “molecular” field in energy units. Due to both electronic and vibronic factors, the degeneracy, g_{HS} , of an excited HS state is necessarily larger than the degeneracy, g_{LS} , of a ground LS one. The additional term of the ligand field proportional to thermal energy $k_B T$ is substantiated by the internal entropy effects. From a thermodynamic standpoint, the physical meaning of h is the Gibbs free energy difference per molecule between the fully HS and LS phases, corresponding to the chemical potential difference between the HS and LS species. Consequently, in this problem, the total energy of the pseudospin array is assumed to be due to elastic interactions involving nearest-neighbor sites under the effect of an external “field.” The equilibrium temperature, T_{eq} , at which one has a 1:1 mixture of HS and LS complexes, is obtained by canceling the effective ligand-field (3), leading to $T_{\text{eq}} = \Delta/k_B \ln g$, depending only on the energy difference in the ligand field Δ and the relative degeneracy of the SCO states g .

Following the same procedure as established in Ndiaye and Boukheddaden [16], we initially determine the mechanical equilibrium of the system in a fixed electronic configuration before subsequently analyzing the resultant Ising-like model. First of all, the local distance r_{ij} that appears in the potential energy (1) is replaced by an average homogeneous variable r assuming the translational invariance of this quantity on the lattice. The resulting elastic potential is expanded in the vicinity of the minimum with respect to the nearest-neighbors (nn) distance, r , up to the third term of a series (anharmonic approximation). The general expression of this “mean-field” elastic potential is given in Sec. II of the SI along with the detailed calculations of the average lattice spacing at mechanical equilibrium, whose expression is given by $r_{\text{eq}} = a_{\text{HL}} + \frac{\delta a}{2}m$, where $m = \frac{1}{N} \sum_{i=1}^N s_i$ denotes the magnetization per spin.

Inserting now the expression of the equilibrium bond length r_{eq} instead of r_{ij} into the expanded version of the elastic energy (see Appendix B), we find that at mechanical equilibrium, the total energy of SCO system (1) as an Ising-like Hamiltonian,

$$\mathcal{H} = \sum_{(ij)} (C_0 + C_1(s_i + s_j) + C_2 s_i s_j) - h \sum_i s_i, \quad (4)$$

where C_0 is reference energy, C_1 and h are external effective fields, and C_2 denotes an intermolecular interaction parameter, whose expressions are

$$C_0 = -\frac{1}{8}\gamma^3 \epsilon m(m^2 + \frac{3}{2}) + \frac{1}{4}\gamma^2 \epsilon (m^2 + \frac{1}{2}), \quad (5)$$

$$C_1 = \frac{1}{16}\gamma^3 \epsilon m(3m^2 + 1) - \frac{1}{4}\gamma^2 \epsilon m, \quad (6)$$

$$C_2 = -\frac{3}{16}\gamma^3 \epsilon m + \frac{1}{8}\gamma^2 \epsilon, \quad (7)$$

where, $\gamma = b\delta a$. Each coefficient is decomposed into components that contain harmonic (in bold notation) and anharmonic contributions.

The derived model was examined using three approaches: the Monte Carlo (MC) method, the molecular field approximation, and the Bethe-Peierls (BP) approximation. The key focus of this study is to assess the degree of correspondence between these approximations and actual physical phenomena.

III. RESULTS AND DISCUSSION

In the nearest-neighbor molecular field approximation, the Hamiltonian assumes the form

$$\mathcal{H}_{\text{MF}} = \frac{zN}{2}C_0 - \frac{zNm^2}{2}C_2 - h_{\text{eff}} \sum_i s_i, \quad (8)$$

where $h_{\text{eff}} = -zC_1 - zmc_2 + h$. The thermodynamic and magnetic properties of a crystal that contains N lattice sites can be determined from the canonical partition function

$$Z_{\text{MF}} = e^{-\frac{zN}{2}\beta C_0 + \frac{zNm^2}{2}\beta C_2} \cdot [2 \cosh(\beta(h_{\text{eff}}))]^N. \quad (9)$$

Hence, we obtain the (Curie-Weiss) equation of states

$$m = \frac{1}{N\beta} \frac{\partial}{\partial h_{\text{eff}}} \ln(Z_{\text{MF}}) = \tanh(\beta h_{\text{eff}}), \quad (10)$$

which is the trademark of the mean-field approximation for the Ising model.

In the BP approximation, the Hamiltonian (4) takes the following form:

$$\begin{aligned} \mathcal{H}_{\text{BP}} = & - \sum_{i=1}^z (-C_0 - C_1(s_i + s_0) - C_2s_is_0) \\ & - hs_0 - h \sum_{i=1}^z s_i - h_1 \sum_{i=1}^z s_i. \end{aligned} \quad (11)$$

We consider a specific spin s_0 with its z nearest neighbors. When writing the Hamiltonian, the interaction between the central spin s_0 and its z nearest neighbors is taken into account exactly, while the interaction of these neighbors with other spins in the lattice is taken into account through a mean molecular field h_1 .

The partition function, Z_{BP} , of this cluster of $z + 1$ spins is

$$\begin{aligned} Z_{\text{BP}} = & Z_+ + Z_- \\ = & e^{\beta(h+zC_1+zC_0)} \cdot [2 \cosh(\beta(C_2 + h + C_1 + h_1))]^z \\ & + e^{-\beta(h+zC_1-zC_0)} \cdot [2 \cosh(\beta(-C_2 + h + C_1 + h_1))]^z. \end{aligned} \quad (12)$$

The magnetization variables $\langle s_0 \rangle$ and $\langle s_i \rangle$ are expressed in terms of Z_{BP} :

$$\langle s_0 \rangle = \frac{Z_+ - Z_-}{Z_{\text{BP}}} \quad \text{and} \quad \langle s_i \rangle = \frac{\partial \ln Z_{\text{BP}}}{z \partial \beta h_1}. \quad (13)$$

The condition $\langle s_0 \rangle = \langle s_i \rangle = m$ and the definition of magnetization m lead to the following system of nonlinear coupled

equations:

$$\begin{cases} e^{2\beta(C_1(1-z)+h_1)} = \left[\frac{\cosh(\beta(C_2+h+C_1+h_1))}{\cosh(\beta(-C_2+h+C_1+h_1))} \right]^{z-1}, \\ m = \frac{Z_+ - Z_-}{Z_{\text{BP}}}. \end{cases} \quad (14)$$

Besides, the BP approximation allows the determination of the correlation factor $r = \langle s_0 s_i \rangle$, which brings information about the nn fluctuations along the thermal transition. This quantity is obtained through the simple relation $\langle s_0 s_i \rangle = \frac{\partial \ln Z_{\text{BP}}}{z \partial \beta C_2}$, which leads to the expression given in Appendix C. This result plays an important role in determining two-point occupation probabilities, such as $(n_{+-} + n_{-+})$, corresponding to the probability of finding two nn spins in HS-LS or LS-HS configuration, as well as others, n_{++} and n_{--} , which correspond to HS-HS and LS-LS pairs, respectively. In fact, it is quite easy to demonstrate that $n_{\text{HL}} = n_{+-} + n_{-+} = \frac{1-r}{2}$, as already introduced in a previous BP study of the Ising-like Hamiltonian by one of the authors [17]. In particular, in the case of molecular field theory, one has $n_{\text{HL}} = \frac{1-m^2}{2}$.

In scenarios where molecules exhibit clustering behavior or antiferromagnetic order as the heating curve progresses, the degree of this clustering can be quantified using the MC correlation factor [18] $r = \frac{1}{zN} \sum_{i=1}^N s_i \sum_{j=1}^z s_j$, where j index runs over the neighbors of site i . Notably, it is expected in the case of antiferro order (plateau regions), the quantity $n_{\text{HL}} = \frac{1-r}{2}$ exhibits a maximum (reaching 1 in the case of a perfect order), while it collapses to 0 in the pure LS and HS phases. It is important to distinguish this situation from that of the disordered state, which appears at $m = 0$, at which also the number of HS-LS nn increases, but reaches at maximum, the value $n_{\text{HL}} = 1/2$.

The previous system of self-consistent equations (14) is solved numerically, using the following parameters values: $\Delta = 1000$ K, $\epsilon = 500$ K, and $\ln g = 7$ and we set $k_B = 1$. For weakly cooperative SCO systems, the outcomes of the MC, BP, and the molecular field approximation coincide, as shown in Fig. 1. The thermally induced spin transition occurs smoothly following two-degenerate levels of Boltzmann statistics with no signs of a phase transition. However, as γ increases, the situation changes significantly. Specifically, for $\gamma = 0.75$, the molecular field approximation predicts an abrupt transition, while the MC simulations, based on the Metropolis algorithm and the BP method, lead to a two-step transition, with a certain deviation from each other (see Fig. 2). It is important to recall that the two-step phase transition behavior in spin-crossover materials was first experimentally observed in Ref. [19] and then has been repeatedly reproduced several times by other authors [13,20–22] over the last few decades. The mechanism underlying these unusual spin conversions was initially theoretically studied on the basis of the cooperative molecular distortion model whose authors clearly predicted the elastic nature of this phenomenon [23]. Qualitative and quantitative theories based on Ising-like Hamiltonians [24,25] and elastic interaction models [6,11,26] were later developed repeatedly. The physical origin of this multistep transition can be evidenced from the analysis of the short-range interaction parameter, C_2 , given in Eq. (7). According to the structure of BP Hamiltonian [Eq. (11)], $C_2 > 0$ (respectively, $C_2 < 0$) promotes antiferroelastic (respectively, ferroelastic) interactions and similarly

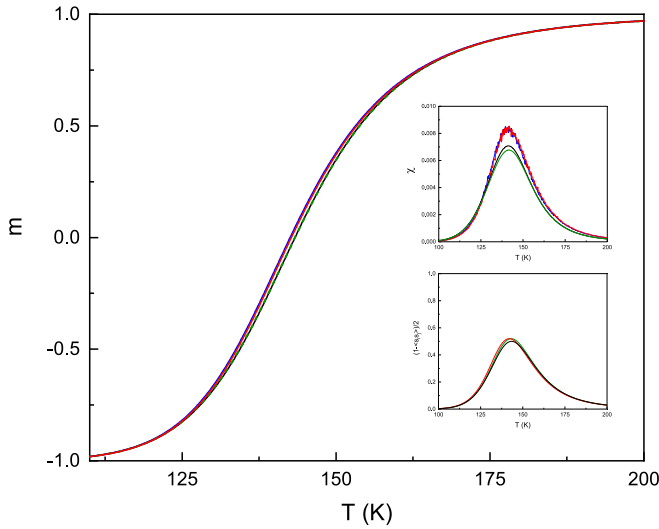


FIG. 1. Thermal transition was calculated for $\gamma = 0.3$ by three methods: molecular field approximation (black curve), BP approximation (green curve), and Monte Carlo method [red (heating) and blue (cooling) curves]. The top and down inserts are, respectively, the magnetic susceptibility χ and the proportion of HS-LS nearest neighbors $n_{\text{HL}} = (1 - r)/2$ obtained in molecular field, BP approximation, and MC simulations, represented with the same color code as above.

for the long-range interaction, $(zC_1 - h_1) < 0$, which favors, in the present case, long-range ferroelastic interactions. Depending on the values of γ , the magnetization dependence of these parameters changes significantly, as evidenced in Fig. 7 in the Appendix. In particular, C_2 is found to be positive in

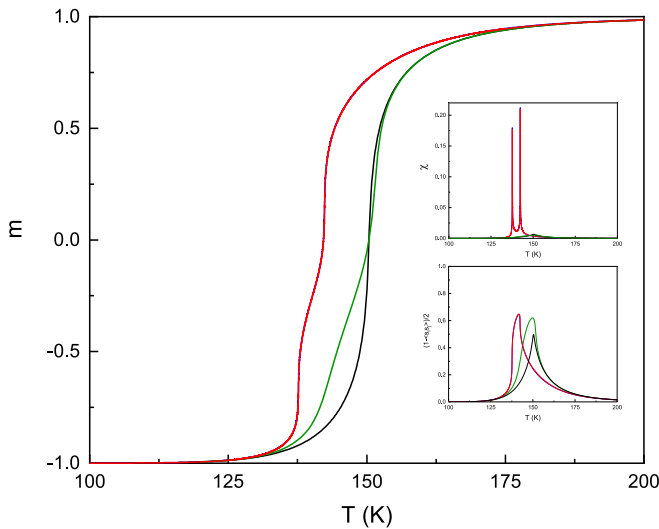


FIG. 2. Thermal transition was calculated for $\gamma = 0.75$ by three methods: molecular field approximation (black curve), BP approximation (green curve), and Monte Carlo method [red (heating) and blue (cooling) curves]. The top and down inserts are, respectively, the magnetic susceptibility χ and the proportion of HS-LS nearest neighbors $n_{\text{HL}} = (1 - r)/2$ obtained in molecular field, BP approximation, and MC simulations, represented with the same color code as above.

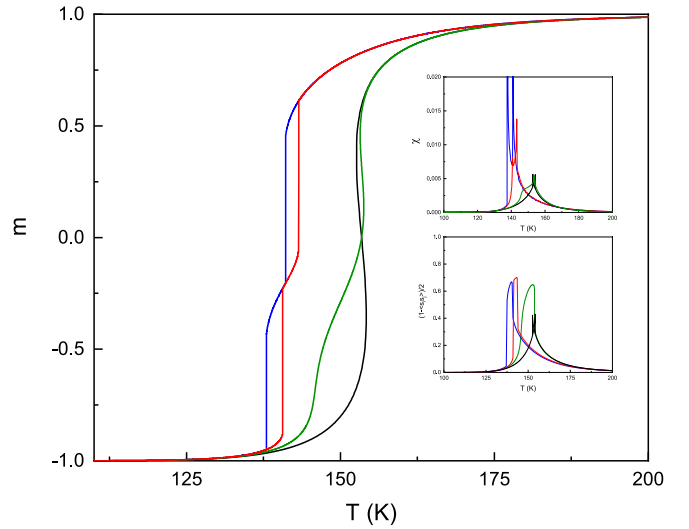


FIG. 3. Thermal transition was calculated for $\gamma = 0.84$ by three methods: molecular field approximation (black curve), BP approximation (green curve) and Monte Carlo method [red (heating) and blue (cooling) curves]. The top and down inserts are respectively the magnetic susceptibility χ and the proportion of HS-LS nearest neighbors $n_{\text{HL}} = (1 - r)/2$ obtained in molecular field, BP approximation and MC simulations, represented with the same color code as above.

a wide spectrum of values of m , which stabilizes the HS-LS neighbors above the threshold value $\gamma = 2/3$. The two-step transition behaviors obtained in the MC and BP approaches in Figs. 2–5 are then due to competition between long-range ferro and short-range antiferro interactions, which generate elastic frustration in the system, as well as the appearance of two peaks in the magnetic susceptibility. Probably the first time such a situation has been observed in an experiment [27].

An increase in γ leads to an even more pronounced discrepancy in the calculation outcomes, as illustrated in Fig. 3. The molecular field approximation predicts a standard hysteresis loop, whereas the Monte Carlo simulations indicate the presence of a double-loop hysteresis. However, the BP approximation shows the onset of a two-step transition in the low-spin region, while retaining a hysteresis-like response in the HS region.

Figure 4 illustrates the spatial organization of the spin states in steady state for $m = -0.217$ and $T = 140.84$ K, corresponding to the data of Fig. 3. Here, the red (blue) dots denote the HS (LS) molecules. The size of the system is 100×100 , with periodic boundary conditions. A clear AF-like order appears in the system at this temperature, although mixed with some disorder due to the presence of antiphase boundaries.

As illustrated in Fig. 5 for $\gamma = 1.1$ the molecular field approximation and Monte Carlo calculation demonstrated the hysteresis behavior but shifted to the lower temperature region for MC simulation, due to the dynamical character of the technique, compared to the molecular field and BP approaches, which deal with stationary states. The BP approximation shows a double-hysteresis transition, but with asymmetrical loops, located in the narrow transition region. As vibrational processes in molecules become more pronounced, the

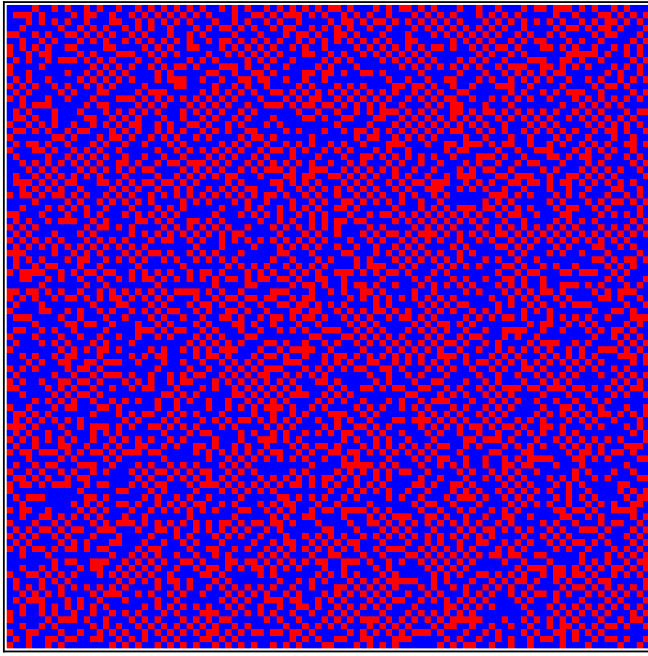


FIG. 4. Example of snapshot showing the spatiotemporal configuration of 100×100 lattice at $m = -0.217$, $T = 140.84$ K, and $\gamma = 0.84$. Red (blue) squares represent HS (LS) sites.

mean-field approximations lose their applicability. The BP approximation remains applicable in the region of two-step and double-hysteresis transitions. However, this approximation works with some lag in γ relative to MC simulations. In the inserts of Figs. 3 and 5, only stable solutions are kept in the molecular field and the BP approximations.

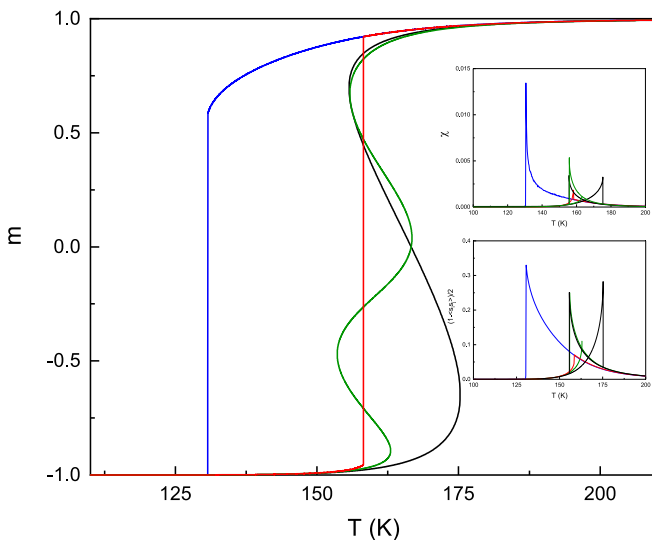


FIG. 5. Thermal transition was calculated for $\gamma = 1.1$ by three methods: molecular field approximation (black curve), BP approximation (green curve), and Monte Carlo method [red (heating) and blue (cooling) curves]. The top and down inserts are respectively the magnetic susceptibility χ and the proportion of HS-LS nearest neighbors $n_{HL} = (1 - r)/2$ obtained in molecular field, BP approximation, and MC simulations, represented with the same color code as above.

These findings are generally consistent with the experimental results reported for the spin-crossover molecular material family [7,9,10,12,13,28].

Our theory is a powerful tool for describing the diverse behaviors exhibited by spin-crossover solid materials. However, its underlying principles are conceptually straightforward. Molecules, treated as two-level units with degenerate states, interact via an isotropic anharmonic medium, wherein the distance between them depends on the magnetic state of the molecules.

IV. CONCLUSION

In summary, we have analyzed an original Hamiltonian that models the SCO phenomenon comprising two energetic contributions: the two-state molecular electronic term and the third-order expansion of the intermolecular Morse potential in deviations from the static positions. This elastic Hamiltonian is mapped into an Ising-like model with state-dependent field-like and interaction coefficients. In our meticulous examination of the conditions of occurrence of phase transitions in spin-crossover materials, we quantitatively compared the outcomes derived from the MC simulation methods with those obtained from the molecular field and BP approximations. Despite the existence of deep discrepancies between the mean-field approximations and the MC technique, the obtained results are very rich and allow for the description of several experimental situations.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

APPENDIX A: MORSE POTENTIALS

Figure 6 shows the Morse potentials as a function of the distance between the metal centers of two interacting molecules for the three cases HS-HS, HS-LS, and LS-LS.

The potential minimum shifts to the right as the interacting molecules switch from a LS-LS to HS-HS configuration.

APPENDIX B: MEAN-FIELD ELASTIC POTENTIAL AND EQUILIBRIUM DISTANCE

The Morse elastic potential (1) is rewritten considering a homogeneous nn distance r between the spin states, leading to

$$V_{\text{elas}} = \epsilon \sum_{\langle ij \rangle} (1 - \exp(-b(r - a_{ij})))^2. \quad (\text{B1})$$

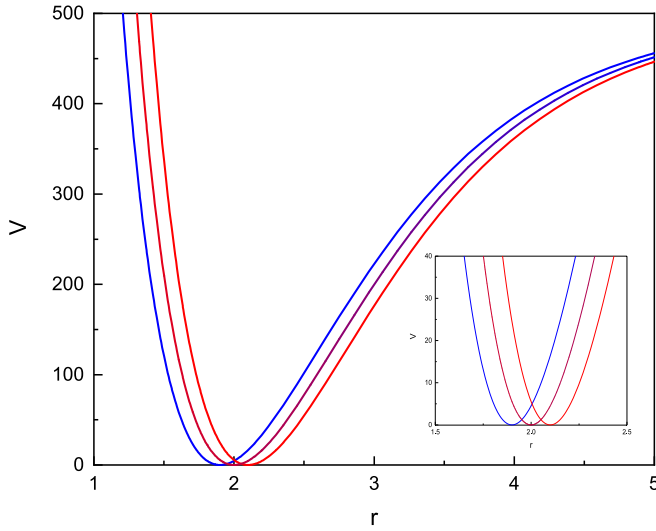


FIG. 6. Morse potentials as a function of the distance between the metal centers of two interacting molecules for three cases HS-HS (red color), HS-LS (a linear color gradient), and LS-LS (blue color) calculated for $\epsilon = 500$, $b = 1$, $a_{HL} = 2$, $\delta a = 0.2$.

1. Determination of r_{eq}

Expanding the square brackets, we obtain the expression

$$V_{elas} = \epsilon \sum_{\langle ij \rangle} (1 - 2 \exp(-b(r - a_{ij})) + \exp(-2b(r - a_{ij}))). \quad (B2)$$

The mechanical equilibrium is obtained by minimizing (B2) with respect to r ,

$$\sum_{\langle ij \rangle} (2b \exp(-b(r - a_{ij})) - 2b \exp(-2b(r - a_{ij}))) = 0 \quad (B3)$$

or

$$2b \sum_{\langle ij \rangle} \left(\frac{\exp(ba_{ij})}{\exp(br)} - \frac{\exp(2ba_{ij})}{\exp(2br)} \right) = 0. \quad (B4)$$

This leads to the general relation involving r_{eq} and averages of nn equilibrium distances, a_{ij}

$$\exp(-br_{eq}) = \frac{\sum_{\langle ij \rangle} \exp(ba_{ij})}{\sum_{\langle ij \rangle} \exp(2ba_{ij})}. \quad (B5)$$

Depending on the desired degree of approximation, r_{eq} may depend only on the averages of fictitious spins $\langle s_i \rangle$ and $\langle s_j \rangle$ or also on the nn spin-spin correlations $\langle s_i \times s_j \rangle$ correlations. The previous expression is equivalent to

$$\exp(-br_{eq}) = \frac{\langle \exp(ba_{ij}) \rangle}{\langle \exp(2ba_{ij}) \rangle}, \quad (B6)$$

where $\langle \dots \rangle$ denotes the average over the lattice. Here, we chose to neglect the contribution of spin-spin correlations to the expression of the equilibrium bond length, r_{eq} , which places the calculations in the frame of pure mean-field theory, in which $\langle \exp(ba_{ij}) \rangle = \exp(b\langle a_{ij} \rangle)$. Consequently, the previous expression leads to

$$r_{eq} = a_{HL} + \frac{\delta a}{2} m, \quad (B7)$$

with $\langle s \rangle = m$ is the average fictitious net magnetization.

2. Anharmonic expansion of the elastic potential

Let us expand the potential (B1) in a series in the vicinity of point a_{ij} to terms of the third order

$$V_{anh} = \epsilon \sum_{\langle ij \rangle} ((b(r - a_{ij}))^2 - (b(r - a_{ij}))^3). \quad (B8)$$

Substituting r_{eq} (B7) in Eq. (B8) we get

$$V_{anh}(r_{eq}) = \epsilon \sum_{\langle ij \rangle} \left(\left(b \left(\frac{\delta a}{2} m - \frac{\delta a}{4} (s_i + s_j) \right) \right)^2 - \left(b \left(\frac{\delta a}{2} m - \frac{\delta a}{4} (s_i + s_j) \right) \right)^3 \right). \quad (B9)$$

Opening the brackets and taking into account $s_i^2 = s_j^2 = 1$ and $s_i^3 = s_i$, as well as the notation for the coefficients C_0 , C_1 , and C_2 , we obtain

$$V_{anh} = \sum_{\langle ij \rangle} (C_0 + C_1(s_i + s_j) + C_2 s_i s_j). \quad (B10)$$

APPENDIX C: EXPRESSION FOR THE CORRELATION FACTOR

The expression for the correlation factor derived as $r = \langle s_0 s_i \rangle = \frac{\partial \ln Z_{BP}}{z \partial \beta C_2}$,

$$r = \frac{-\cosh[\beta(C_1 - C_2 + h + h_1)]^{z-1} \sinh[\beta(C_1 - C_2 + h + h_1)]}{\cosh[\beta(C_1 - C_2 + h + h_1)]^z + \exp 2\beta(zC_1 + h) \cosh[\beta(C_1 + C_2 + h + h_1)]^z} + \frac{\exp 2\beta(zC_1 + h) \cosh[\beta(C_1 + C_2 + h + h_1)]^{z-1} \sinh[\beta(C_1 + C_2 + h + h_1)]}{\cosh[\beta(C_1 - C_2 + h + h_1)]^z + \exp 2\beta(zC_1 + h) \cosh[\beta(C_1 + C_2 + h + h_1)]^z}. \quad (C1)$$

APPENDIX D: MONTE CARLO SIMULATION

The MC simulations were conducted through the standard Metropolis algorithm on a square lattice with periodic boundary conditions, enabling individual pseudospin flips.

The two-dimensional square lattice size N was chosen as $N = 100 \times 100$, which is a good choice between the influence of system size effects and the speed of calculation. Every simulation was running for $N_{MC} = 3100$ Monte Carlo steps per spin,

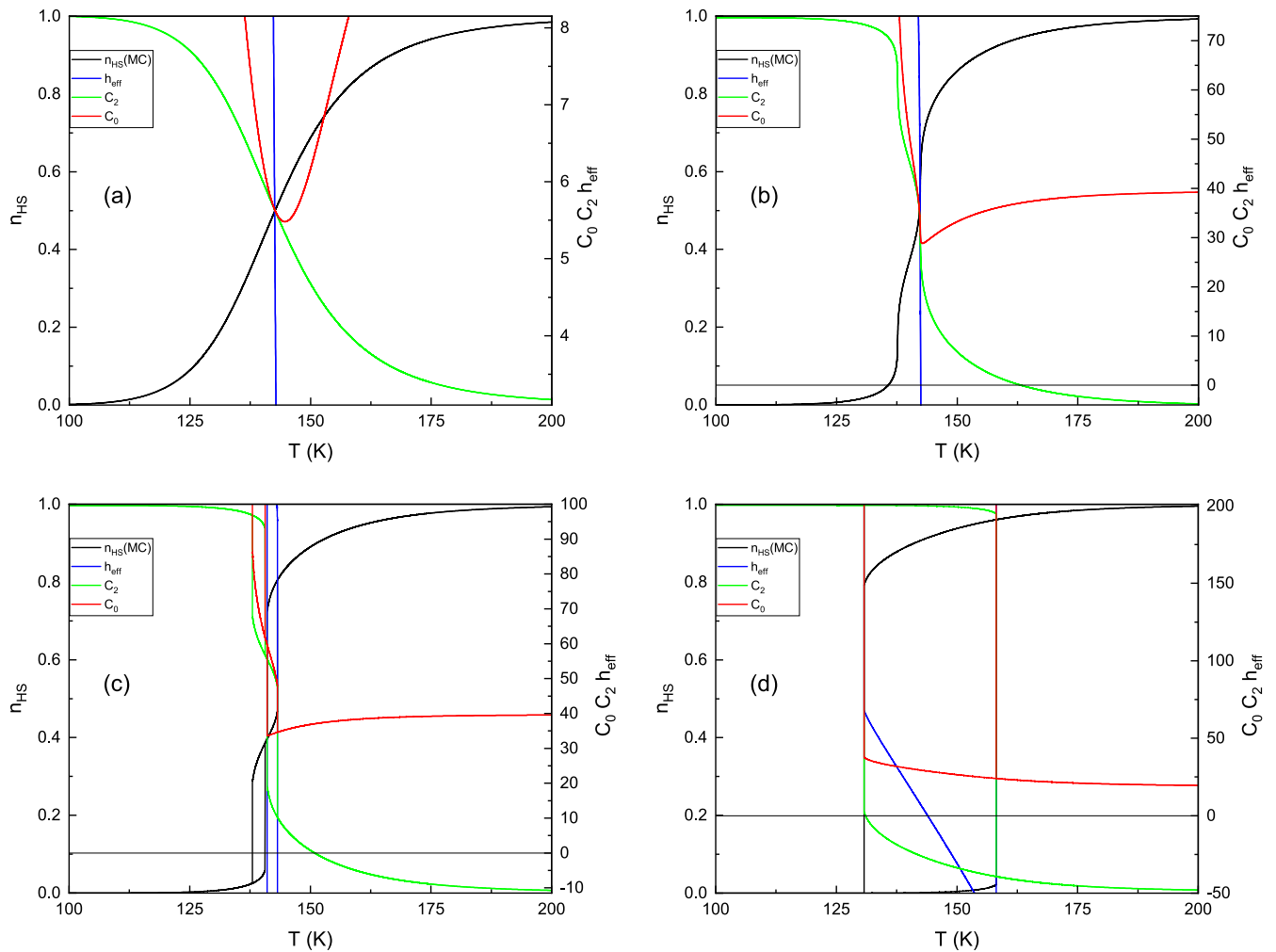


FIG. 7. Demonstration of how n_{HS} and parameters of the problem depends on the temperature. The values of γ are 0.3 (a), 0.75 (b), 0.84 (c), 1.1 (d).

which means $N \times N_{\text{MC}}$ Metropolis steps per temperature step. First 100 Monte Carlo steps were not considered and taken to reach equilibrium. The simulations are started in the HS state (all spins up) at an elevated temperature ($T = 300$ K). The thermal properties of the system are determined by first cooling down from the HS state at 300 K to 1 K and then by warming up to the HS state at 300 K, with 0.01 K increments. The waiting time between two MC measurements is 10 000 of flipping while the number of MC steps used for the statistics is $2 \times 350 \times 10 \times 3000$.

Intermolecular interaction calculated by the MC method

In Fig. 7, as a supplement to Figs. 1–3 and 5 in the main text, we show the parameter of the intermolecular interaction C_2 [see Eq. (7)], the reference energy C_0 [see Eq. (5)] and the effective field h_{eff} calculated by the Monte Carlo method as functions of temperature. As can be seen in Eq. (7), the temperature dependence of the intermolecular interaction parameter, C_2 , reflects the linear dependence of this parameter on the magnetic state of the system.

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