Cooperative Phenomena in Spin Crossover Systems

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Within the framework of a realistic multi-band $p-d$- model, we derived an effective Hamiltonian to describe the exchange interaction effects near the spin crossover in magnetic Mott-Hubbard insulators under pressure. It is shown that single-ion mechanism of spin crossover under change of the crystal field does not lead to a thermodynamic phase transition, however, at $T = 0$ a quantum phase transition appears. It has been found that the cooperativity leads to a modification of the quantum phase transition to a first-order phase transition and the appearance of metastable states of the system. The pressure - temperature phase diagram has been obtained to describe the magnetization and high-spin population near the spin crossover of the Mott's insulators with d^6- ions.

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I. INTRODUCTION

A spin crossover (SCO) was discovered by Combi almost 80 years ago[1], but so far it attracts the attention of researchers. Primarily, the interest to SCO- systems was connected with the hope to design free-inertial molecular two-state switches which can be used to store and process information in fast computational devices. Development of nanotechnology prompts the study of this phenomenon in order to use certain properties of the SCO in the quantum transport and creation of a new generation of sensors and displays[2]. Spin systems with crossover include extensive class of materials: organometallic complexes, organic radicals, inorganic salts and transition metal oxides. The SCO phenomenon is associated with the energy level crossing of two different spin multiplets of magnetic ion under changing of some external parameters, i.e. temperature, pressure, light irradiation, etc. Due to its cooperative nature, the SCO connects the micro- and macroscopic properties of the system. Sometimes the SCO is considered as a phase transition of a special type, the so-called supercritical transitions[3]. A nice example of a planetary scale of a spin state transition is the SCO in ferropericlase at high pressure[4], that probably takes place in the Earth's mantle[4–8]. To date, the effect of pressure and temperature on the spin transition was described in terms of various approaches and approximations. One of the most common approaches is based on the Landau theory of phase transitions[9]. The second successful approach is based on the Ising model[2,10–34]. A third approach is the microscopic one[35]. Each of these approaches has strengths and weaknesses (for discussion see Refs.[36,37]).

In general, SCO results from a competition of the Hund intra-atomic exchange interaction and the crystal field value determined by surroundings ions. At first glimpse it is a problem of individual ion in a given crystal field. The external or chemical pressure changes the crystal field and induces the SCO as well as all other external effects changing the interatomic distance. Cooperative effects in such systems result in different hysteresis phenomena and play an important role in the practical applications and understanding of their nature. One can single out several essential types of interaction between metal ions, namely, electron-phonon, quadrupole and exchange interaction.

Cooperativeness in magnetic insulators is usually caused by interatomic exchange interaction. However, this mechanism does not work in SCO- systems with the ground state being low-spin (LS) singlet ion level. The magnetic cations of organometallic complexes are connected to each other by chemical bridges, and cooperative effects are realized through elastic interaction. In the literature, we have found a few works that discuss coope-

rative magnetic effects through the exchange interaction between the excited high-spin (HS) states (see., i.e.,[38,39]). In all these studies the form of the exchange interaction is postulated phenomenologically, as Heisenberg exchange interaction with empirical parameters. In the last decade a lot of works based on the density functional theory have appeared to describe the SCO phenomenon. For example, the SCO properties and phase diagram have been obtained for $[Fe(PM-BIA)_2(NCS)_2]$ compound[40]. Recently, various models with elastic constant depending on the distance between the structural elements have been studied by methods of molecular dynamics[41,42] and Monte Carlo simulations[43,44]. Along with the use of static pressure there are also some studies on the effect of impact pressure on the spin state of coordination complexes, such as $[Fe(phen)_2(NCS)_2]$[45]. It was shown that a relatively low pressure pulse of 0.02 GPa is capable to induce an almost complete conversion of the spin on the hysteresis branches. Such effects may be applied to a spin state switching devices by using SCO- materials.

Since the direct overlap of d- orbitals of neighboring ions in the transition metal oxides is small, the main mechanism of the exchange interaction in these compounds is the Kramers-Anderson indirect exchange (superexchange). Besides, the interplay of electronic hopping between neighbouring ions with the orbital structure of different spin multiplets also results in spin-orbital cooperative effects in strongly correlated transition metal oxides[46]. The most common and versatile approach to the SCO problem is based on the effective Hamiltonian. Within this approach, all these materials are treated from a single point of view. However, when two different spin multiplets are close, effective interaction between the magnetic cations may be far from the Heisenberg interaction, and the effective Hamiltonian should be obtained from a multielectron microscopic approach.

The present work is devoted to a neat derivation of the effective Hamiltonian for transition metal oxides with SCO and study influence of arising cooperative effects on formation of the physical features of these materials as well. By using the effective Hamiltonian approach, we study effect of the exchange interaction on the SCO. In this way the orbital HS- and LS- states of the $3d$- ion are described in terms of one-half pseudospin. To obtain all parameters of the effective Hamiltonian, we applied the hybrid multielectron LDA+GTB approach[47], where GTB means a generalized tight binding method. The use of projection Hubbard operators, as part of the LDA+GTB method, yield new terms in the effective Hamiltonian, previously not considered. They are responsible for the exciton type interaction. This opens up interesting possibilities for further research of both equilibrium and nonequilibrium phenomena in the SCO- systems, for instance, interaction with radiation.

The paper is organized as follows. In Sec. 2 we derive the effective Hamiltonian for the multi-band model of strongly correlated 3d-oxides. In Sec. 3 the SCO phenomena is studied in the mean field approximation. In Sec. 4 the results of numerical simulations are presented. In Conclusion we discuss the obtained results.

II. EFFECTIVE HAMILTONIAN APPROACH TO THE SPIN CROSSOVER IN MAGNETIC INSULATORS

For the transition metal (TM) compounds with the predominant type of ionic bonding (i.e. oxides, halides, etc.), strong electron correlations determine the insulator and magnetic properties. The commonly accepted minimal model for description of such compounds is a multi-band $p-d$- model[48–50]. This model explicitly takes into account the Coulomb interaction of d- electrons of the TM- ion. The Hamiltonian of the model can be written as,

$$\mathcal{H} = \mathcal{H}_d + \mathcal{H}_p + \mathcal{H}_{pd}. \tag{1}$$

Here the first term, $\mathcal{H}_d = \sum_{i,\lambda,\sigma} \varepsilon_d^\lambda d^\dagger_{i,\lambda,\sigma} d_{i,\lambda,\sigma} + \mathcal{H}_d^{Coulomb}$, describes the d-electrons in the crystal field: ($\lambda = xy, yz, zx, x^2-y^2, z^2$) and their Coulomb interaction. The second term, $H_p = \sum\limits_{j,\alpha,\sigma} \varepsilon_p^\alpha p^+_{j\alpha\sigma} p_{j\alpha\sigma} + \sum\limits_{\langle j,j'\rangle} \sum\limits_{\alpha,\beta,\sigma} t_{pp}^{\alpha\beta} \left(p^+_{j\alpha\sigma} p_{j'\beta\sigma} + h.c.\right)$, with the hopping integral being $t_{pp}^{\alpha\beta}$, describes p-electrons of oxygen or other ligands involved in σ- and π-coupling ($\alpha, \beta = x, y, z$). The third term, $\mathcal{H}_{pd} = \sum_{\langle i,j\rangle,\sigma} (t_{pd}^{\lambda\alpha} d^\dagger_{i\lambda\sigma} p_{j\alpha\sigma} + h.c)$, characterizes the hybridization of the cation-anion states.

In this approach the Coulomb energy of p-electrons is usually neglected. However, if necessary, it can be easily taken into account within the framework of our LDA+GTB- approach (see below). Multi-band $p-d$- model, with all Coulomb interactions: $d-d$, $p-p$, and $p-d$ being included, was discussed in[51].

An important advantage of this multi-orbital model is the ability to form different many-electron states (terms) of the transition metal's ion. These terms are characterized by different values of the spin, $0 \leq S \leq 5/2$, and the orbital angular momentum. For d^n- ion in the crystal field, the ground state depends on the relationship between the Hund exchange constant, J_H, and the crystal field, $10Dq$. In some cases, the amount of cation-anion hybridization makes its contribution to the stability of HS/LS terms[52].

The magnitude of the crystal field depends on the interatomic distance and it is changed when the external pressure or "chemical pressure" is applied. The chemical pressure appears when isovalent substitution occurs in a series of solid solutions or stretching. For ionic crystals energy terms of d^n- electron configurations in a cubic crystal field have been obtained numerically. The results are presented by the so-called Tanabe-Sugano diagrams[53].

In the framework of the LDA+GTB approach, parameters of the Hamiltonian (1) are obtained from the first principles. In order to adequately account electron correlations, the cluster approach of GTB method is applied[51].

In the GTB approach the crystal lattice is divided into clusters ("elementary cells"), and the total Hamiltonian can be written as, $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$, where $\mathcal{H}_0 = \sum_f \mathcal{H}_c(f)$ is related to the contribution of all noninteracting clusters, and $\mathcal{H}_1 = \sum_{fg} \mathcal{H}_{cc}(f,g)$ describes hopping and interaction between clusters.

The Hamiltonian, $\mathcal{H}_c(f)$, can be diagonalized exactly. We denote by $|p\rangle$ its eigenstates with the energy E_p. Next step is to introduce the Hubbard X-operators. They are defined in a standard way[54]: $X_f^{pq} = |p\rangle\langle q|$. Algebra of X- operators is determined by the multiplying rule, $X_f^{pq} X_g^{rs} = \delta_{fg}\delta_{qr} X_f^{ps}$, and the completeness condition, $\sum X_f^{pp} = 1$. The indices p and q, being collective indices, contain a set of the following quantum numbers: the number of electrons n_p per unit cell, an irreducible representation Γ , that describes the transformation of the orbital part of the wave function under action of the point symmetry group of the given crystal, the magnitude of the spin, S, and its projection, m_S. Thus, one can write, $|p\rangle = |n_p; \Gamma; m_\Gamma; S; m_S\rangle$.

It is assumed that for the neighbor cells the eigenstates are orthogonal. If not, for instance, as in the case when two adjacent clusters share a common oxygen, one needs to use the orthogonalization procedure, employing the Wannier functions instead of the group of oxygen orbitals. For the first time such a procedure has been proposed for the three-band $p-d$- model in[55] and generalized to a multi-band model in[56].

Since the Hubbard operators form a linearly independent basis, any local operator can be expressed as a linear combination of X- operators. For instance, a single-electron annihilation operator, $a_{f\nu\sigma}$, in a f-cell with the band index ν, can be written as, $a_{f\nu\sigma} = \sum_{pq} |p\rangle\langle p|a_{f\nu\sigma}|q\rangle\langle q| = \sum_{pq} \gamma_{\nu\sigma pq} X_f^{pq}$. In the X-operators representation the Hamiltonian (1) takes the form,

$$\mathcal{H} = \sum_{f,p} (E_p - \mu n_p) X_f^{pq} + \sum_{f \neq g} \sum_{mn} t_{fg}^{mn} X_f^{\dagger m} X_g^n, \tag{2}$$

where μ is the chemical potential and $t_{fg}^{mn} = \sum_{\sigma\nu\nu'} T_{fg}^{\nu\nu'} \gamma_{\nu\sigma}^*(m) \gamma_{\nu'\sigma}(n)$. Here $T_{fg}^{\nu\nu'}$ are the hopping matrix elements in the basis of the orthogonalized Wannier functions. The SCO occurs in the case of the energy level crossing of the two different spin states under the influence of external factors.

In what follows, we generalize the method of projection operators, developed for the Hubbard model[57], to obtain the effective Hamiltonian from (2), by excluding the interband hopping integral through the dielectric gap. We define for two nearest neighbor sites i and j the projection operator P_1 as,

$$P_1 = \sum_p (X_i^{pp} + X_j^{pp}) + \sum_{p.p'} X_i^{pp} X_j^{p'p'}. \tag{3}$$

In the r.h.s. of the Eq. (3) only those states $|p\rangle$ and $|p'\rangle$ are taken into consideration, for which the number of electrons per unit cell, n_p, is more (or less) than it follows from the electrical neutrality condition. As one can see, the operators P_1 and $P_2 = 1 - P_1$ satisfy the following identity: $P_a P_b = \delta_{ab} P_a$, where $a, b = 1, 2$.

Let us consider the auxiliar Hamiltonian, $\mathcal{H}_\eta = \mathcal{H}' + \eta\mathcal{H}''$, where $\mathcal{H}' = P_1\mathcal{H}P_1 + P_2\mathcal{H}P_2$ and $\mathcal{H}'' = P_1\mathcal{H}P_2 + P_2\mathcal{H}P_1$, with η being a formal parameter. At the end of computation we set $\eta = 1$. Using the identity $\mathcal{H} = \sum_{a,b} P_a \mathcal{H} P_b$, one can show that $\mathcal{H}_\eta|_{\eta=1} = \mathcal{H}$. Here $\mathcal{H}'$ contains interatomic electron hopping inside the individual Hubbard subbands, while $\mathcal{H}''$ describes the interband electron hopping via the large Mott-Hubbard band.

We employ the method of operator perturbation theory to eliminate the processes with the interband hopping. The essence of the operator perturbation theory is that, using a canonical

transformation, $\tilde{\mathcal{H}}_\eta = \exp(-i\eta U)\mathcal{H}_\eta \exp(i\eta U)$, one can choose the operator U so that the terms of the Hamiltonian linear in η, $\tilde{\mathcal{H}}_\eta$, i. e. contributions of the interband hopping, vanish. As one can show, this condition results in the following equation for the operator U:

$$\mathcal{H}'' + [\mathcal{H}', U] = 0. \tag{4}$$

One can see that the condition $\tilde{\mathcal{H}} = \tilde{\mathcal{H}}_\eta|_{\eta=1}$ can be recast as,

$$\tilde{\mathcal{H}} = \mathcal{H}' + \frac{i}{2}[\mathcal{H}'', U]. \tag{5}$$

Using the results obtained in[57], we found

$$\tilde{\mathcal{H}} = P_1\mathcal{H}P_1 + P_2\mathcal{H}P_2 - \frac{1}{E_{ct}}[P_1\mathcal{H}P_2, P_2\mathcal{H}P_1], \tag{6}$$

where $E_{ct} = \langle P_2 H P_2\rangle - \langle P_1 H P_1\rangle$ is the charge transfer energy that determines the insulator gap E_g. The first two terms in (6) describe the electron hopping in the conductivity and valence band. The last term results in the effective exchange Hamiltonian given by superexchange interaction. This approach has been developed for the Hubbard model[57] and has been used with X- operators for La_2CuO_4 and $FeBO_3$[58].

Gathering all results together, one can show that the effective Hamiltonian in the representation of spin operators, $\mathbf{S}_i$, and pseudospin operators, $\boldsymbol{\tau}_i$, becomes

$$\mathcal{H}_{eff} = \sum_{\alpha,\beta=1,2}\sum_{\langle i,j\rangle} J_{\alpha\beta}\big(\mathbf{S}_i^\alpha\cdot\mathbf{S}_j^\beta + \frac{\xi}{4}n_i^\alpha n_j^\beta\big)p_i^\alpha p_j^\beta + \big(f(P)-\varepsilon_0\big)\sum_i \tau_i^z + \mathcal{H}_{exiton}. \tag{7}$$

The summation is performed over neighboring sites on a lattice with coordination number z. The first term describes the exchange contribution to the Heisenberg Hamiltonian, n_i^α stands for operators of the particles on the i-site, the parameter $\xi = -1, 3$ corresponds to the antiferromagnetic and ferromagnetic ordering, respectively. The projection operators, $p_i^\alpha = (1/2)(1+\lambda_\alpha\tau_i^z)$, are defined in the subspace of eigenstates of the pseudospin operator, $\tau_i^z|\alpha\rangle = \lambda_\alpha|\alpha\rangle$, with the eigenvalues being $\lambda_1 = 1$ and $\lambda_2 = -1$. The index α takes the value 1 for the HS- state and 2 for the LS- state of the system thus $p^1|1\rangle = |1\rangle$, $p^1|2\rangle = 0$, $p^2|1\rangle = 0$, $p^2|2\rangle = |2\rangle$. The second term in Eq.(7) describes variation in the relative energy of electronic configurations for LS- and HS- states under the influence of the applied pressure P. In Eq. (7) we set $\varepsilon_0 = \Delta_s/2$, where $\Delta_s = E_{LS} - E_{HS}$ is the energy gap between the LS- and HS- states at zero pressure. Here $f(P)$ denotes a pressure contribution to the spin gap ε_0. We consider situation when at $P = 0$ HS is stable ($\varepsilon_0 > 0$).

In the representation of spin and pseudospin operators, the Hamiltonian (7) has the form:

$$\mathcal{H}_{eff} = \sum_{\alpha,\beta=1,2}\sum_{\langle i,j\rangle} J_{\alpha\beta}\big(\mathbf{S}_i^\alpha\cdot\mathbf{S}_j^\beta + \frac{\xi}{4}n_i^\alpha n_j^\beta\big)\cdot \big(1+\lambda_\alpha\tau_i^z + \lambda_\beta\tau_j^z + \lambda_\alpha\lambda_\beta\tau_i^z\tau_j^z\big) + \big(f(P)-\varepsilon_0\big)\sum_i \tau_i^z + \mathcal{H}_{exiton}. \tag{8}$$

The third term in Eq. (7) includes the interaction of the excitonic type. The most simple form it takes for two-level system. In this case orbital and spin singlet, $|S\rangle$, stand for the LS-state, and the HS- state is described by spin triplet, $|M\rangle$, with the spin projections being, $M = 0, \pm 1$. Thus, $\mathcal{H}_{exiton}$ can be written as,

$$\mathcal{H}_{exiton} = J_{exiton}\sum_M\sum_{\langle i,j\rangle}\Big(\tau_i^+\tau_j^- X_i^{M,S}X_j^{S,M} + \tau_i^-\tau_j^+ X_i^{S,M}X_j^{M,S} - (-1)^M(\tau_i^+\tau_j^+ X_i^{M,S}X_j^{M,S} + \tau_i^-\tau_j^- X_i^{S,M}X_j^{S,M})\Big) \tag{9}$$

where on the i-site the Hubbard operators $X_i^{M,S}$ and $X_i^{S,M}$ describe the excitations in the spin subspace of the system from the singlet state to the triplet state with the projection of the spin M, and vice versa. The operators τ_i^+ and τ_i^- have the same meaning for the orbital part of the wave functions.

Note that the interaction between the spin and orbital degrees of freedom has long been studied in the literature in the Kugel-Khomskii

model[59]. Our Hamiltonian contains formally similar combination of the pseudospin and spin operators, but the physical origin of pseudospin states here is different from the single electron analogues in the Kugel-Khomskii model.

The Hamiltonian (7) can be generalized by including the phonon interaction between TM-ions and spin-orbit interaction. The phonon contribution is described by[59],

$$\mathcal{H}_{e-ph} = J_1 \sum_{\langle i,j \rangle} \tau_i^x \tau_j^x + J_3 \sum_{\langle i,j \rangle} \tau_i^z \tau_j^z \qquad (10)$$

where the coupling constants J_1 and J_3 are determined by the interaction of different phonon modes of the lattice. The spin-orbit interaction in the highest order of the perturbation theory leads to the mixture of the the LS- and HS- states caused by tunneling of the system through a potential barrier between the LS- and HS-states. The corresponding Hamiltonian can be written as[60],

$$\mathcal{H}_{so+tunneling} = J_x \sum_i \tau_i^x. \qquad (11)$$

In recent years the unusual properties of supramolecules, containing spin-active coordinated TM- ions of the iron group, have increasingly drawn the attention of researchers. These systems exhibit both, the thermal SCO and the SCO, arising under the impact of pressure, or as a result of the light irradiation of the sample (LIESST- effect). The LIESST spin transition, HS →LS, being induced by the interaction of the vibronic levels of different multiplicity, is often accompanied by hysteresis[61].

Irradiation of frozen $[Fe(ptz)_6](BF4)_2$ sample at a wavelength of 514 nm results in spin-allowed transitions ${}^1A_1 \to {}^1T_1$. The excited state would relax back to the initial singlet state, unless the spin-orbit interaction had provided intersystem transitions in the triplet states, ${}^3T_2$ and ${}^3T_1$. These states overlap with the quintet, ${}^5E$, which then relaxes into a metastable state ${}^5T_2$. The latter can exist indefinitely at low temperatures, since the potential barrier separates it from the ground state ${}^1A_1$. To reverse LIESST, the low-lying state ${}^3T_1$ should exist. This state is an intermediate in the two intersystem crossing and can decay into ${}^5T_2$ and ${}^1A_1$. Therefore, by irradiating such a state at a closest infrared wavelength transition: ${}^5T_2 \to {}^5E$ (752,7 nm for $[Fe(ptz)_6](BF4)_2$), the reverse transition in singlet ${}^1A_1$ can be carried out.

The terms $\mathcal{H}_{exiton}$ and $\mathcal{H}_{e-ph}$ (see Eqs. (9) and (11)) are directly related to the LIESST-effect and can be used for description and simulation of the SCO in supramolecule systems.

III. MEAN FIELD APPROXIMATION

In what follows we consider an antiferromagnetic system ($\xi = -1$, $J_{\alpha\beta} > 0$) and restrict ourselves for simplicity by consideration only these interactions, writing the effective Hamiltonian as,

$$\mathcal{H}_{eff}^{s\tau} = \sum_{\alpha,\beta=1,2} \sum_{\langle i,j \rangle} J_{\alpha\beta} \big(\mathbf{S}_i^\alpha \cdot \mathbf{S}_j^\beta - \frac{1}{4} n_i^\alpha n_j^\beta \big) p_i^\alpha p_j^\beta + \big(f(P) - \varepsilon_0 \big) \sum_i \tau_i^z. \qquad (12)$$

The method can be applied in a straightforward way also in the ferromagnetic case, $\xi = 3$ and $J_{\alpha\beta} < 0$. As concerns possible pseudispin ordering we restrict ourselves in this paper to the case of pseudospin ferromagnetisn. It means that each ion has the same spin state.

In the mean field approximation the effective Hamiltonian, $\mathcal{H}^{MF}$, can be written as (for detail see Appendix A),

$$\mathcal{H}^{MF} = \mathcal{H}_0 - \sum_i \sum_{\alpha,\beta=1,2} z J_{\alpha\beta} n_\alpha n_\beta S_\beta \langle \mathbf{m}^\beta \rangle \mathbf{S}_i^\alpha - \Delta_{eff} \sum_i \tau_i^z, \qquad (13)$$

where $\mathbf{m}_i^\alpha = (0, 0, m_i^\alpha)$ is a unit vector, so that one can write the staggered magnetization $\langle \mathbf{S}_i^\alpha \rangle = S_\alpha \langle \mathbf{m}_i^\alpha \rangle$,

$$\mathcal{H}_0 = \sum_i \sum_{\alpha,\beta=1,2} \Big(\nu_{\alpha\beta} n_\alpha n_\beta \langle \mathbf{m}^\alpha \rangle \langle \mathbf{m}^\beta \rangle - \frac{1}{2} \Delta_{\alpha\beta} n_\alpha (1 - n_\beta) \Big), \qquad (14)$$

$$\Delta_{eff} = \frac{1}{2} \sum_{\alpha,\beta=1,2} \Delta_{\alpha\beta} \lambda_\beta n_\alpha + (\varepsilon_0 - f(P)). \qquad (15)$$

Here $\nu_{\alpha\beta} = z J_{\alpha\beta} S_\alpha S_\beta$, and

$$\Delta_{\alpha\beta} = z J_{\alpha\beta} \Big(\langle \mathbf{S}^\alpha \rangle \langle \mathbf{S}^\beta \rangle + \frac{1}{4} N_\alpha N_\beta \Big). \qquad (16)$$

We denote by $n_\alpha = \langle p_i^\alpha \rangle = (1/2)(1 + \lambda_\alpha \langle \tau^z \rangle)$ the HS- state ($\alpha = 1$) and LS- state ($\alpha = 2$) fraction.

Thus, the Hamiltonian, $\mathcal{H}^{MF}$, given by Eq. (13) can be considered as the effective Hamiltonian for description of SCO as pressure, temperature or both, are changed.

The computation of thermodynamic averages yields the sublattice magnetization m and

uniform pseudospin order parameter $\tau = \langle \tau^z \rangle$

$$m_\alpha = B_{S_\alpha}(\beta \sum_{\alpha'=1,2} \nu_{\alpha\alpha'} n_\alpha n_{\alpha'} m_{\alpha'}), \quad (17)$$

$$\langle \tau^z \rangle = \tanh\left(\beta\Delta_{eff} + \ln\sqrt{g}\right) \quad (18)$$

where $m_\alpha \equiv \langle m_i^\alpha \rangle$, $\beta = 1/k_B T$, $g = g_{HS}/g_{LS}$ being ratio of the degeneracy of HS- and LS-states, and

$$B_S(x) = \left(1 + \frac{1}{2S}\right) \coth\left(\left(1 + \frac{1}{2S}\right)x\right) - \frac{1}{2S}\coth\left(\frac{x}{2S}\right) \quad (19)$$

is the Brillouin function.

The population of HS- and LS- state is found to be

$$n_{HS} = n_1 = \frac{1 + \tanh\left(\beta\Delta_{eff} + \ln\sqrt{g}\right)}{2}, \quad (20)$$

$$n_{LS} = n_2 = \frac{1 - \tanh\left(\beta\Delta_{eff} + \ln\sqrt{g}\right)}{2}. \quad (21)$$

IV. IMPACT OF COOPERATIVE EFFECTS ON THE SPIN CROSSOVER

We find that in the mean field approximation the SCO in the transition metal compounds can be described by the effective Hamiltonian (13). The population of HS- and LS- state is described by self-consistent system of the transcendental equations: Eqs. (17), (20), (21).

In what follows we restrict ourselves by consideration of the case $S_2 = 0$. It is convenient to introduce a new parameter q, writing $N_\alpha = qS_\alpha$. Further, we assume $q = 2$. Let us denote $m = m_1$, $n = n_1$ and $S = S_1$, $J_{22} = J_{12} = J_{21} = 0$, $J = J_{11}$. Then Eqs. (17), (20), (21) can be rewritten as,

$$m = B_S(\beta\nu m n^2), \quad (22)$$

$$n = \frac{1 + \tanh\left(\beta\Delta_{eff} + \ln\sqrt{g}\right)}{2}, \quad (23)$$

where

$$\Delta_{eff} = \frac{\nu}{2}(1 + m^2)n + \varepsilon_0 - f(P). \quad (24)$$

The effective Hamiltonian (13) can be recast as,

$$\mathcal{H}^{MF} = \mathcal{H}_0 - \sum_i \mathbf{B}\cdot\mathbf{S}_i - \Delta_{eff}\sum_i \tau_i^z, \quad (25)$$

where $\mathbf{B} = zJSn^2\langle\mathbf{m}\rangle$ and

$$\mathcal{H}_0 = \frac{N\nu m^2}{2}n(3n-1) - \frac{N\nu}{2}n(1-n). \quad (26)$$

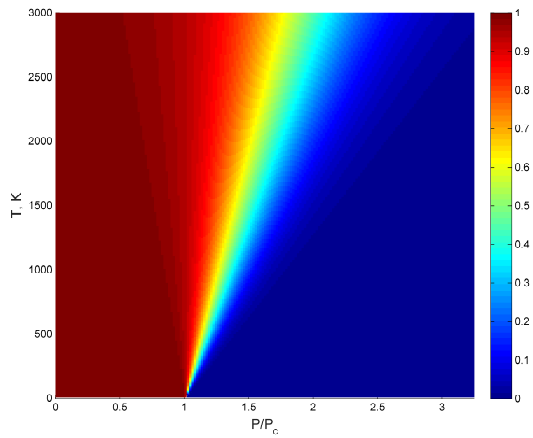

Figura 1: Color online) HS-state population vs. pressure and temperature in absence of the exchange interaction ($J = 0$).

The critical pressure, P_c, corresponds to the energy level crossing of HS- and LS- states and satisfies the equation, $\varepsilon_0 - f(P_c) = 0$. Its magnitude is determined by a competition of the crystal field and the intraionic Hund exchange. For TM- ions in the cubic and tetrahedral crystal field, the explicit magnitudes of P_c are obtained in[62–65]. Further we assume $f(P) = aP$, so that one can write $\varepsilon_0 = aP_c$.

Below, in our numerical simulations, the parameters are chosen as follows: $S = 2$, $z = 6$, $g = 15$, $J = 28\,\mathrm{K}$, $a = 80\,\mathrm{K/Gpa}$ and $P_c = 55\,\mathrm{Gpa}$. The pressure is measured in units of P_c and the temperature in inits of J.

First we consider the behavior of the system described by Eqs. (22) - (24) in the absence of exchange interaction, $J = 0$. In this case the magnetization $m = 0$. The results of numerical simulations are presented in Fig. 1. Similar figures have been obtained previously in[7,66–71]. At $T = 0$, one can observe a sharp jump in the population of the HS-state at the crossover point. In the thermodynamic limit this is related to the quantum phase transitions with the order parameter being the Berry phase[72]. With increasing of the temperature the quantum phase transition becomes a smooth crossover.

A. Low temperature limit

In the limit of $T \to 0$, we succeeded to obtain the analytical solution given by the following multi-valued function (blue-dashed lines

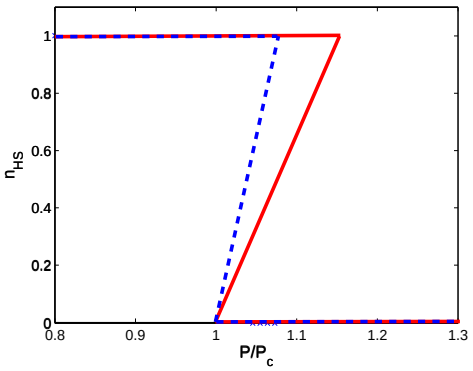

Figura 2: (Color online) The HS fraction vs. pressure. Red line ($T = 0, m = 1$) and blue dashed line ($T = 0, m = 0$).

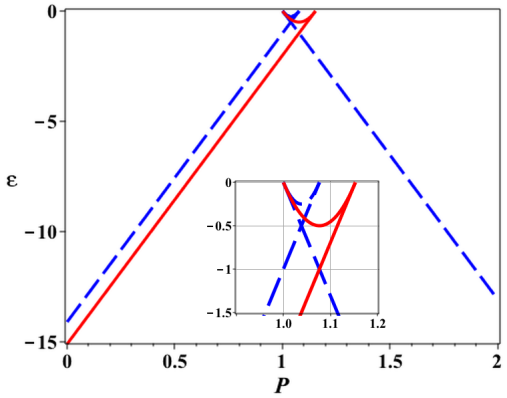

Figura 3: (Color online) Energy of system, $\varepsilon = E/E_0$, at zero temperature vs pressure: $m = 0$ (blue dashed curve), $m = 1$ (red curve).

for $m = 0$ and red lines for $m = 1$ in Fig. 2):

$$n = \begin{cases} 1, & 0 \le P \le P_m \\ \alpha_m(P-1), & 1 < P < P_m \\ 0, & P \ge 1 \end{cases} \tag{27}$$

where $P_m = 1 + \alpha_m^{-1}$ and

$$\alpha_m = \frac{2aP_c}{\nu(1+m^2)}. \tag{28}$$

The interval of pressure, $\Delta P_m = \alpha_m^{-1}$, corresponds to the region of critical behavior of a physical system in which hysteresis phenomena are significant. For the chosen parameters we find $\Delta P_0 \approx 4{,}2\,\mathrm{GPa}$ and $\Delta P_1 \approx 8{,}4\,\mathrm{GPa}$. Note that in the absence of cooperativity ($J = 0$) width of this domain is zero, $\Delta P_m = 0$.

At zero temperature the ground state of the system is defined by the minimum of its energy,

$$E = -E_0\big((1+m^2)n^2 + \alpha_0(1-P)(2n-1)\big), \tag{29}$$

where $E_0 = N\nu/2$.

In Fig. 3 the dimensionless energy of the system, $\varepsilon = E/E_0$, is depicted at zero temperature. It is clear from Fig. 3 that SCO at zero temperature is the first order HS-LS transition at critical pressure $P_0 > P_C$, $P_0 = 1{,}076$ for the chosen set of parameters.

B. Numerical solutions

At fixed temperature and volume, the equilibrium state of a system is characterized in terms of the Helmholtz free energy, $F = E - TS$. The computation of the free energy per site yields

$$F = H_0 - k_B T \ln Z_s - k_B T \ln Z_\tau, \tag{30}$$

where

$$H_0 = \frac{\nu m^2}{2} n(3n-1) - \frac{\nu}{2} n(1-n). \tag{31}$$

The partition functions of the spin and pseudospin subsystems being Z_s and Z_τ, respectively, are given by

$$Z_s = \frac{\sinh\left(\left(1+\frac{1}{2S}\right)\beta\nu m n^2\right)}{\sinh\left(\frac{1}{2S}\beta\nu m n^2\right)}, \tag{32}$$

$$Z_\tau = 2\sqrt{g}\cosh(\beta\Delta_{eff} + \ln\sqrt{g}). \tag{33}$$

In Fig. 4 $P - T$ phase diagrams of HS- state population n_{HS} (a) and magnetization m (b), corresponding to the minimum free energy F (30), are depicted.

In Fig. 5 all the possible self-consistent solutions of the system Eqs. (22) - (23) for the above set of parameters, marked with red circles for the magnetization m and blue crosses for the populations of HS- state n_{HS} for some specific values of external pressure (see. below) as function of temperature are depicted. Those solutions that correspond to the minimum of the free energy are connected by solid lines (the red line for the magnetization m, blue - for the population of the HS- state n_{HS}). The remaining solutions are metastable. From Fig. 4 it is clear that due to the exchange interaction J the ground magnetically ordered state is maintained until $P_0 > P_C$ despite the fact that in the single-ion picture when $P > P_C$ the ground

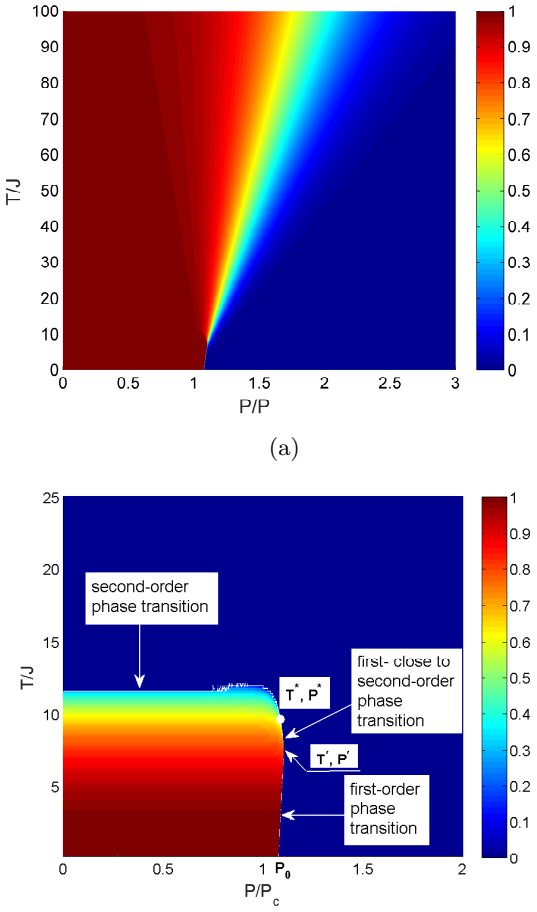

Figura 4: (Color online) $P-T$ phase diagram corresponding to the minimum of the free energy: (a) HS-state population, (b) magnetization. Here T^*, P^* is the tricritical point, and T', P' is the reentrant transition critical point.

state is a non-magnetic LS- state. The increase of P_0 vs P_C is related to the additional energy gain of the HS state vs LS due to the interatomic exchange coupling. At $P > P_0$ the magnetic ground state is transform to a non-magnetic by the first-order transition. Crossing of two energies that are typical for the first-order phase transitions are clear visible in Fig. 3. In the range of pressure $P \leq P_0$ (Fig. 4b, 5a and 5b) with increasing temperature the system undergoes the second-order phase transition to the paramagnetic state. On the $P-T$ diagrams of a physical system (Fig. 4) the existence of a singular point, the so-called tri-critical point (T^*, P^* in Fig. 4b), in which the second-order phase transition line continuously passes in line of the first-order phase transitions, is well visible. At $P > P_0$ the ground state of the system is not magnetic. With increasing of temperature the magnetic HS- state is populated, and due to the phase transition of the first-order the antiferromagnetic phase is restored (Fig. 5c and 5d) as energetically more favorable for $P \leq P'$. Thus, due to the cooperative interaction, J, in systems with spin crossover under pressure the reentrant transition at $P_0 < P < P'$ may exist. With further increase of temperature the system goes into the paramagnetic state by a phase transition of the second-order if $P \leq P^*$ and of the first-order close to the second if $P^* < P \leq P'$ (Fig. 5d). With increasing pressure at $P > P_C$ an energy interval between the ground non-magnetic LS- state and the nearest excited magnetic HS- state is increased. When $P > P'$ (Fig. 4f), the thermal energy required for the HS- state population to the desired extent become comparable with the value of the exchange interaction J and magnetic order disappears.

V. CONCLUSION

Previously the effect of interatomic Coulomb and exchange interaction have been studied in paper[73], where quite similar mean-field solutions have been obtained. We study the effect of pressure on SCO that has not been discussed in[73].

Cooperative effects in the SCO systems, where the role of the controlling parameter is carried out by external pressure, lead to an unusual modification of the system. The magnetic ordering can be suppressed by external pressure, and near of the quantum critical point a region of metastable states arises.

In the absence of exchange interaction and magnetization at $J = 0$, there is a sharp change in the population of the HS- state at the crossover point at $T = 0$, which corresponds to a quantum phase transition[72]. With increasing temperature, the quantum phase transition at $T = 0$ smeared into a smooth transition, a crossover. In the presence of cooperativity in the form of an exchange interaction, the quantum phase transition with an increase in temperature is first reconstructed into a thermodynamic transition of the first and then of the second order. The appearance of phase transitions of the first-order with discontinuities of the magnitude of the magnetic moment and the population of ionic terms due to large (up to 10 %) differense of the HS and LS ionic radii results in a break of the volume of the crystal as a fun-

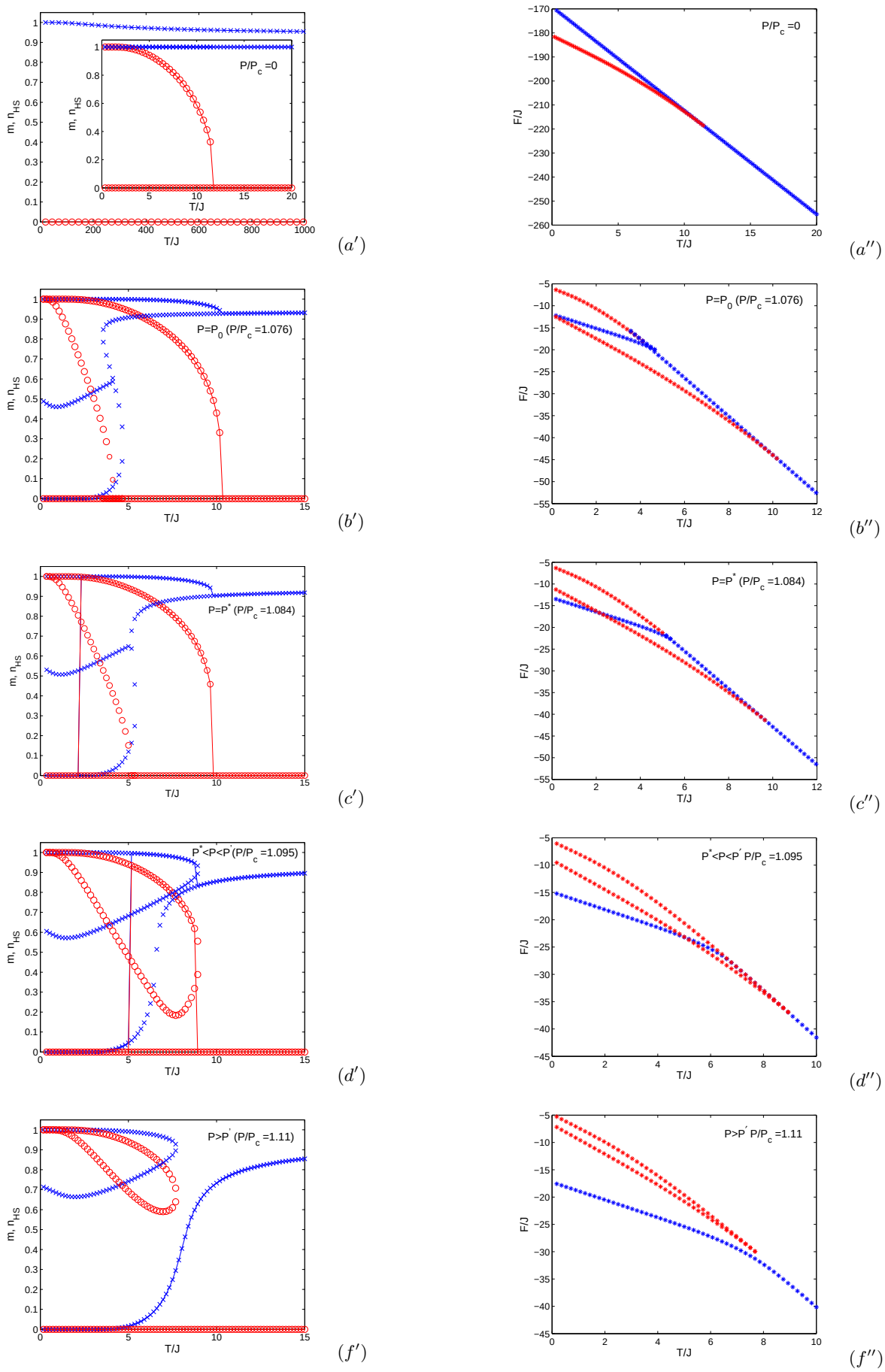

Figura 5: (Color online) Solutions of Eqs. (22) - (23) for different values of external pressure as function of temperature. Couples of solutions for the magnetization (circles) and the population of the HS- state (crosses), for which the thermodynamic potential (right panel) has the lowest value, are connected by a solid line. In the right panel marked in blue those values of the Helmholtz free energy that are correspond to $m = 0$, and in red $m = 0$.

ction of temperature and pressure. Metastable states contributes to the appearance of a hysteresis loop and a kind of irreversibility of the process of phase transformation. Features in the behavior of the volume with increasing pressure result in anomalies in the modulus of elasticity and the speed of sound propagation in materials with a spin crossover. The $P-T$ phase diagram obtained by us can be used to analyze and describe the experimental data and measurements of magnetic, structural, and various thermodynamic quantities in magnetically ordered substances with a spin crossover under pressure. The direct massage to experimentalists from this paper is that at low temperatures spin crossover under high pressure is indeed the first order phase transition if the sample temperature is below the tricritical temperature $T^* \approx 0{,}8T_N$.

In SCO- compounds, local bistable states, i.e., HS- and LS- states, have different molecular sizes, and the elastic interaction is important. The elastic interaction, induced by the lattice distortion due to the difference of the molecular size, causes an effective long-range interaction. In realistic compounds the short-range interaction also plays a role in phase transitions. For example, if we consider the usual Lennard-Jones potential between molecules which depends on the spin states, the model has both elastic and short-range interactions[74]. Competition and interplay between the short-range and long-range interactions are interesting topics in phase transitions[75–80,82,83]. In the pure short-range model, clustering of the ordered phase takes place near the critical temperature, leading to the divergence of the correlation length of the order parameter. However, the long-range interaction suppresses the generation of domains, and the configuration is uniform even at the critical temperature[81]. This effect should be experimentally observable as an absence of critical opalescence[81–83]. Phase transitions in such systems belong to the mean-field universality class.

In[84,85] authors showed that short-range interactions favor nearest-neighbor HS-LS pairs (called antiferromagnetic-like), and a long-range (elastic) interaction favoring all molecules in the same spin state (all LS or all HS, called ferromagnetic-like). In our work we obtained that short-range exchange interaction could favor both anti and ferromagnetic HS/LS- state ordering. It can be seen from expression (8) that the magnetic ordering determines the orbital pseudospin ordering. Thus, an antiparallel ordered orientation of the spin magnetic moments of neighboring lattice sites of the crystal (sAFM) at $J > 0$ contributes to the ferromagnetic ordering of the pseudospin moments (τFM). Conversely, a parallel ordered orientation of the spin magnetic moments of neighboring sites (sFM) contributes to the antiferromagnetic ordering of the pseudospin moments (τAFM). In addition, for $J < 0$, states with the same orientation of the spin and pseudospin moments (sFM-τFM, sAFM-τAFM) are favorable from the viewpoint of the energy minimum.

In the experiment the independent variables are the pressure and temperature. In this paper, analysis of the SCO system was carried out for the fixed volume, using the Helmholtz free energy. However, even in this limited approach, one can determine the main properties of the SCO. The potential difference with the general case, that includes the possible change of the system volume, will be only quantitative. In order to take into account the latter effect, one should consider the Gibbs thermodynamic potential instead of the Helmholtz free energy. This work is in progress.

X-ray diffraction data indicate that in the region of critical pressures where magnetic, electronic and spin transitions are observed the structural transformations occur, but in different crystals they occur according to different scenarios[86]. In the magnetically ordered phase, at $T < T_N$, a sharp volume jump is observed, and at $T > T_N$ only a smooth change, while in most cases the symmetry of the crystal is conserved. So at $T = 300K$ for $(MgFe)O$ and $GdFe_3(BO_3)_4$ for which $T_N < 300K$ there is a smooth change in volume. For $FeBO_3$ ($T_N = 348K$) there is a jump without hysteresis within the measurement error. For the orthoferrites ($NdFeO_3$, $LaFeO_3$, $PrFeO_3$) and hematite Fe_2O_3 with high T_N, there is a jump with hysteresis[86].

Summarizing, the main new results of this paper are the following: due to interatomic exchange interaction spin crossover at $T < T^* < T_N$ is the first order phase transition and accompanied by a sharp volume change. For $T^* < T < T_N$ spin crossover is the second order phase transition. For $T > T_N$ spin crossover is not a phase transition.

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Apéndice A: MEAN FIELD APPROXIMATION

In this section we deduce the effective Hamiltonian in the mean field approximation. We start with the Hamiltonian (7)

$$\mathcal{H}_{eff} = \sum_{\alpha,\beta=1,2} \sum_{\langle i,j\rangle} J_{\alpha\beta}\big(\mathbf{S}_i^\alpha \cdot \mathbf{S}_j^\beta + A_{ij}^{\alpha\beta}\big) p_i^\alpha p_j^\beta + \big(f(P) - \varepsilon_0\big) \sum_i \tau_i^z + \mathcal{H}_{exiton}, \tag{A1}$$

where we set $A_{ij}^{\alpha\beta} = (\xi/4) n_i^\alpha n_j^\beta$. In what follows we neglect by the contribution of the last term, $\mathcal{H}_{exiton}$.

Let us write the spin and pseudospin variables as, $\mathbf{S}_i^\alpha = \langle \mathbf{S}_i^\alpha \rangle + \delta \mathbf{S}_i^\alpha$ and $\tau_i^z = \langle \tau_i^z \rangle + \delta \tau_i^z$. Here $\delta \mathbf{S}_i^\alpha = \mathbf{S}_i^\alpha - \langle \mathbf{S}_i^\alpha \rangle$, $\delta \tau_i^z = \tau_i^z - \langle \tau_i^z \rangle$ and $\langle \dots \rangle$ denotes the average value. In the mean field approximation one neglects by the contribution of the second order terms in the fluctuations, so that

$$(\langle \mathbf{S}_i^\alpha \rangle + \delta \mathbf{S}_i^\alpha)(\langle \mathbf{S}_j^\beta \rangle + \delta \mathbf{S}_j^\beta) \approx \langle \mathbf{S}_i^\alpha \rangle \langle \mathbf{S}_j^\beta \rangle + \delta \mathbf{S}_i^\alpha \langle \mathbf{S}_j^\beta \rangle + \langle \mathbf{S}_i^\alpha \rangle \delta \mathbf{S}_j^\beta, \tag{A2}$$

$$(\langle \mathbf{S}_i^\alpha \rangle + \delta \mathbf{S}_i^\alpha)(\langle \tau_j^z \rangle + \delta \tau_j^z) \approx \langle \mathbf{S}_i^\alpha \rangle \langle \tau_j^z \rangle + \delta \mathbf{S}_i^\alpha \langle \tau_j^z \rangle + \langle \mathbf{S}_i^\alpha \rangle \delta \tau_j^z, \tag{A3}$$

$$(\langle \tau_i^z \rangle + \delta \tau_i^z)(\langle \tau_j^z \rangle + \delta \tau_j^z) \approx \langle \tau_i^z \rangle \langle \tau_j^z \rangle + \delta \tau_i^z \langle \tau_j^z \rangle + \langle \tau_i^z \rangle \delta \tau_j^z. \tag{A4}$$

In the mean field approximation the spins and pseudospins are independent of each other, and its average does not depend on the site. Thus, one can write $\langle \tau_i^z \rangle = \langle \tau^z \rangle$ and $\langle \mathbf{S}_i^\alpha \rangle = \langle \mathbf{S}^\alpha \rangle$.

The antiferromagnetic case can be resolved by introducing two topologically equivalent sublattices, say A and B[87,88]. Then in the mean field approximation one can show that $\langle \mathbf{S}_A \rangle = -\langle \mathbf{S}_B \rangle$.

Using Eqs. (A2) – (A4) in (A1), we obtain

$$\mathcal{H}_{eff}^{s\tau} = -\sum_{\alpha,\beta=1,2} \sum_{\langle i,j\rangle} J_{\alpha\beta}\big(R_{ij}^{\alpha\beta} n_\alpha n_\beta + 2 n_\alpha n_\beta \langle \mathbf{S}^\alpha \rangle \delta \mathbf{S}_j^\beta + 2 R_{ij}^{\alpha\beta} n_\alpha \delta p_j^\beta\big) + \big(f(P) - \varepsilon_0\big) \sum_i \tau_i^z \tag{A5}$$

where $R_{ij}^{\alpha\beta} = \langle \mathbf{S}^\alpha \rangle \langle \mathbf{S}^\beta \rangle + A_{ij}^{\alpha\beta}$, and $n_\alpha = \langle p_i^\alpha \rangle = (1/2)(1 + \lambda_\alpha \langle \tau^z \rangle)$ denotes the HS- state ($\alpha = 1$) and LS- state ($\alpha = 2$) fraction. Here and below for $J_{\alpha\beta}$ and ξ we shall mean only their absolute values.

Substituting $\delta \mathbf{S}_j^\beta = \mathbf{S}_j^\beta - \langle \mathbf{S}^\beta \rangle$, $\delta p_j^\beta = p_j^\beta - n_\beta$ into (A5), we obtain

$$\begin{aligned}\mathcal{H}_{eff}^{s\tau} = &\sum_{\langle i,j\rangle} \sum_{\alpha,\beta=1,2} J_{\alpha\beta}\big(2 n_\alpha n_\beta \langle \mathbf{S}^\alpha \rangle \langle \mathbf{S}^\beta \rangle - R_{ij}^{\alpha\beta} n_\alpha (1 - n_\beta)\big) - \sum_{\langle i,j\rangle} \sum_{\alpha,\beta=1,2} J_{\alpha\beta}\big(2 n_\alpha n_\beta \langle \mathbf{S}^\alpha \rangle \mathbf{S}_j^\beta + R_{ij}^{\alpha\beta} \lambda_\beta n_\alpha \tau_j^z\big) \\ &+ \big(f(P) - \varepsilon_0\big) \sum_i \tau_i^z \end{aligned} \tag{A6}$$

Next, we replace the particle number operator by its average: $n_i^\alpha \to \langle n_i^\alpha \rangle \equiv N_\alpha$ and replace $R_{ij}^{\alpha\beta}$ by $R_{\alpha\beta} = \langle \mathbf{S}^\alpha \rangle \langle \mathbf{S}^\beta \rangle + (\xi/4) N_\alpha N_\beta$. Then, in the approximation of the nearest neihgbors we obtain

$$\begin{aligned}\mathcal{H}_{eff}^{s\tau} = &\frac{z}{2} \sum_i \sum_{\alpha,\beta=1,2} J_{\alpha\beta}\big(2 n_\alpha n_\beta \langle \mathbf{S}^\alpha \rangle \langle \mathbf{S}^\beta \rangle - R_{\alpha\beta} n_\alpha (1 - n_\beta)\big) - \frac{z}{2} \sum_i \sum_{\alpha,\beta=1,2} J_{\alpha\beta}\big(2 n_\alpha n_\beta \langle \mathbf{S}^\alpha \rangle \mathbf{S}_i^\beta + R_{\alpha\beta} \lambda_\beta n_\alpha \tau_i^z\big) \\ &+ \big(f(P) - \varepsilon_0\big) \sum_i \tau_i^z \end{aligned} \tag{A7}$$

Let $\mathbf{m}_i^\alpha = (0, 0, m_i^\alpha)$ be a unit vector, so that $\langle \mathbf{S}_i^\alpha \rangle = S_\alpha \langle \mathbf{m}_i^\alpha \rangle$. Then one can recast the effective mean field Hamiltonian (A7) as follows:

$$\mathcal{H}^{MF} = \sum_i \sum_{\alpha,\beta=1,2} \Big(\nu_{\alpha\beta} n_\alpha n_\beta \langle \mathbf{m}^\alpha \rangle \langle \mathbf{m}^\beta \rangle - \frac{1}{2} \Delta_{\alpha\beta} n_\alpha (1 - n_\beta) \Big) - \sum_i \sum_{\alpha,\beta=1,2} z J_{\alpha\beta} n_\alpha n_\beta S_\beta \langle \mathbf{m}^\beta \rangle \mathbf{S}_i^\alpha - \Delta_{eff} \sum_i \tau_i^z, \tag{A8}$$

where $\nu_{\alpha\beta} = z J_{\alpha\beta} S_\alpha S_\beta$, $\Delta_{\alpha\beta} = z J_{\alpha\beta} R_{\alpha\beta}$ and $\Delta_{eff} = (1/2) \sum_{\alpha,\beta=1,2} \Delta_{\alpha\beta} \lambda_\beta n_\alpha + (\varepsilon_0 - f(P))$.

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