PHYSICAL REVIEW B **96**, 134103 (2017)

Cooperative phenomena in spin crossover systems

Alexander I. Nesterov[*]
CUCEI, Universidad de Guadalajara, Guadalajara, Codigo Postal 44420, Jalisco, Mexico

Yuri S. Orlov[†] and Sergey G. Ovchinnikov[‡]
Kirensky Institute of Physics, Federal Research Center, KSC SB RAS, 660036 Krasnoyarsk, Russia
and Siberian Federal University, 660041 Krasnoyarsk, Russia

Sergey V. Nikolaev[§]
Institute of Engineering and Radio Electronics, Siberian Federal University, 660041 Krasnoyarsk, Russia

(Received 20 February 2017; revised manuscript received 12 August 2017; published 9 October 2017)

Within the framework of a realistic multiband 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 the single-ion mechanism of spin crossover under the change in 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 Mott's insulators with d^6 ions.

DOI: 10.1103/PhysRevB.96.134103

I. INTRODUCTION

A spin crossover (SCO) was discovered by Cambi and Cagnasso almost 80 years ago [1], and it has attracted the attention of researchers ever since. Primarily, the interest in SCO systems has been connected to the hope to design free inertial molecular two-state switches which can be used to store and process information in fast computational devices. The development of nanotechnology has prompted studying this phenomenon to use certain properties of the SCO in quantum transport and to create a new generation of sensors and displays [2]. Spin systems with crossover include extensive classes 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 a magnetic ion with varying 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 a special type of phase transition, the so-called supercritical transition [3]. A nice example of a planetary scale of a spin-state transition is the SCO in ferropericlase at high pressure [4], which probably takes place in the Earth's mantle [4–8]. To date, the effect of pressure and temperature on the spin transition has been described in terms of various approaches and approximations. One of the most common approaches is based on the Landau theory of phase transitions [9]. A 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 between the Hund intra-atomic exchange interaction and the crystal-field value determined by surroundings ions. At first glance, it is a problem of an 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 interactions between metal ions, namely, electron-phonon, quadrupole, and exchange interactions.

Cooperativeness in magnetic insulators is usually caused by the interatomic exchange interaction. However, this mechanism does not work in SCO systems with the ground state being the 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 cooperative magnetic effects through the exchange interaction between the excited high-spin (HS) states (see., e.g., [21,38]). In all these studies the form of the exchange interaction is postulated phenomenologically, as the Heisenberg exchange interaction with empirical parameters. In the last decade many works based on density functional theory have appeared to describe the SCO phenomenon. For example, the SCO properties and phase diagram have been obtained for the $[\mathrm{Fe(PM-BIA)_2(NCS)_2}]$ compound [39]. Recently, various models with the elastic constant depending on the distance between the structural elements have been studied using the methods of molecular dynamics [40,41] and Monte Carlo simulations [42,43]. 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 $[\mathrm{Fe(phen)_2(NCS)_2}]$ [44]. It was shown that a relatively low pressure pulse of 0.02 GPa is capable of inducing an almost complete conversion of the spin on the hysteresis branches.

---

[*] nesterov@cencar.udg.mx

[†] jso.krasn@mail.ru

[‡] sgo@iph.krasn.ru

[§] 25sergeyn@mail.ru

Such effects may be applied to 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). In addition, the interplay of electronic hopping between neighboring ions with the orbital structure of different spin multiplets also results in spin-orbital cooperative effects in strongly correlated transition-metal oxides [45]. 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 studying the influence of arising cooperative effects on the formation of the physical features of these materials. By using the effective Hamiltonian approach, we study the 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 the parameters of the effective Hamiltonian, we applied the hybrid multielectron local-density approximation (LDA) plus generalized tight binding (GTB) approach [46]. The use of projection Hubbard operators as part of the LDA+GTB method yields terms in the effective Hamiltonian not considered previously. They are responsible for the exciton-type interaction. This opens up interesting possibilities for further research into both equilibrium and nonequilibrium phenomena in SCO systems, for instance, interaction with radiation.

This paper is organized as follows. In Sec. II we derive the effective Hamiltonian for the multiband model of strongly correlated $3d$ oxides. In Sec. III the SCO phenomenon is studied in the mean-field approximation. In Sec. IV the results of numerical simulations are presented. In the conclusion we discuss the obtained results.

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

For 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 multiband p-d model [47–49]. This model explicitly takes into account the Coulomb interaction of the 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, $\mathcal{H}_d = \sum_{i,\lambda,\sigma} \varepsilon_d^{\lambda} d_{i,\lambda,\sigma}^{\dagger} d_{i,\lambda,\sigma} + \mathcal{H}_d^{\text{Coulomb}}$, 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, $H_p = \sum\limits_{j,\alpha,\sigma} \varepsilon_p^{\alpha} p_{j\alpha\sigma}^{+} p_{j\alpha\sigma} + \sum\limits_{\langle j,j'\rangle} \sum\limits_{\alpha,\beta,\sigma} t_{pp}^{\alpha\beta} (p_{j\alpha\sigma}^{+} p_{j'\beta\sigma} + \text{H.c.})$, 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, $\mathcal{H}_{pd} = \sum_{\langle i,j\rangle,\sigma} (t_{pd}^{\lambda\alpha} d_{i\lambda\sigma}^{\dagger} p_{j\alpha\sigma} + \text{h.c.})$, 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). The multiband p-d model with all Coulomb interactions (d-d, p-p, and p-d) included was discussed in [50].

An important advantage of this multiorbital 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, $0 \leqslant S \leqslant 5/2$, and the orbital angular momentum. For a 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 a contribution to the stability of HS/LS terms [51].

The magnitude of the crystal field depends on the interatomic distance, and it changes when 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 [52].

In the framework of the LDA+GTB approach, parameters of the Hamiltonian (1) are obtained from the first principles. In order to adequately account for electron correlations, the cluster approach of the GTB method is applied [50].

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 energy E_p. The next step is to introduce the Hubbard X operators. They are defined in the standard way [53]: $X_f^{pq} = |p\rangle\langle q|$. The algebra of the 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, which describes the transformation of the orbital part of the wave function under the 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 neighboring cells the eigenstates are orthogonal. If not, as in the case when two adjacent clusters share a common oxygen, one needs to use the orthogonalization procedure, employing Wannier functions instead of the group of oxygen orbitals. Such a procedure was proposed for the three-band p-d model in [54] and generalized to a multiband model in [55].

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-operator 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 [56], 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

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

On the right-hand side of Eq. (3) only those states $|p\rangle$ and $|p'\rangle$ for which the number of electrons per unit cell n_p is more (or less) than what follows from the electrical neutrality condition are taken into consideration. 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 auxiliary 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 [56], 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 bands. The last term results in the effective exchange Hamiltonian given by the superexchange interaction. This approach has been developed for the Hubbard model [56] and has been used with X operators for La_2CuO_4 and $FeBO_3$ [57].

Gathering all the 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

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

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 the operators of the particles on ith site, and 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 a value of 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 the 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

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

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

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

where on the ith 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 using the Kugel'-Khomskii model [58]. Our Hamiltonian contains a formally similar combination of the pseudospin and spin operators, but the physical origin of pseudospin states here is different from the single-electron analogs in the Kugel'-Khomskii model.

The Hamiltonian (7) can be generalized by including the phonon interaction between TM ions and the spin-orbit interaction. The phonon contribution is described by [58]

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

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 a mixture of 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 [59]

$$\mathcal{H}_{so+\text{tunneling}} = J_x \sum_i \tau_i^x. \tag{11}$$

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 from the impact of pressure or as a result of the light irradiation of the sample (Light Induced Excited Spin State Trapping (LIESST) effect. This phenomenon is due to the interaction of vibronic levels with different multiplicities), which are often accompanied by hysteresis [60].

Irradiation of a frozen [Fe(ptz)$_6$](BF4)$_2$ sample at a wavelength of 514 nm results in spin-allowed transitions $^1A_1 \rightarrow {}^1T_1$. The excited state will relax back to the initial singlet state unless the spin-orbit interaction provides 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 intermediate in the two intersystem transitions and can decay into $^5T_2$ and $^1A_1$. Therefore, by irradiating such a state at the closest infrared wavelength transition, $^5T_2 \rightarrow {}^5E$ [752.7 nm for [Fe(ptz)$_6$](BF4)$_2$], the reverse transition in singlet $^1A_1$ can be carried out.

The terms $\mathcal{H}_{\text{exiton}}$ 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, to considering only antiferromagnetic interactions, writing the effective Hamiltonian as

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

The method can be applied in a straightforward way also in the ferromagnetic case, $\xi = 3$ and $J_{\alpha\beta} < 0$. In regard to possible pseudospin ordering we restrict ourselves in this paper to the case of pseudospin ferromagnetism. This 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 details see the Appendix)

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

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

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

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

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

$$\Delta_{\alpha\beta} = zJ_{\alpha\beta}\left(\langle \mathbf{S}^\alpha \rangle \langle \mathbf{S}^\beta \rangle + \frac{1}{4} N_\alpha N_\beta\right). \tag{16}$$

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 ($\alpha = 2$) fractions.

Thus, the Hamiltonian $\mathcal{H}^{MF}$ given by Eq. (13) can be considered the effective Hamiltonian for the 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 $\tau = \langle \tau^z \rangle$:

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

$$\langle \tau^z \rangle = \tanh(\beta \Delta_{\text{eff}} + \ln \sqrt{g}), \tag{18}$$

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

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

is the Brillouin function.

The populations of HS and LS states are found to be

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

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

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 populations of HS and LS states are described by the self-consistent system of the transcendental equations [Eqs. (17), (20), and (21)].

In what follows we restrict ourselves to the 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 $m = m_1$, $n = n_1$, $S = S_1$, $J_{22} = J_{12} = J_{21} = 0$, and $J = J_{11}$. Then Eqs. (17), (20), and (21) can be rewritten as

$$m = B_S(\beta \nu m n^2), \tag{22}$$

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

where

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

The effective Hamiltonian (13) can be recast as

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

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

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

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 fields, the explicit magnitudes of P_c are obtained in [61–64]. Further, we assume $f(P) = aP$, so that one can write $\varepsilon_0 = aP_c$.

Below, in our numerical simulations, the parameters are set as follows: $S = 2$, $z = 6$, $g = 15$, $J = 28$ K, $a = 80$ K/GPa, and $P_c = 55$ GPa. The pressure is measured in units of P_c, and the temperature is in units 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 were obtained previously in [7,65–70]. 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 [71]. With increasing temperature, the quantum phase transition becomes a smooth crossover.

A. Low-temperature limit

In the limit of $T \to 0$, we succeeded in obtaining the analytical solution given by the following multivalued function (blue dashed line for $m = 0$ and red solid line for $m = 1$ in Fig. 2):

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

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

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

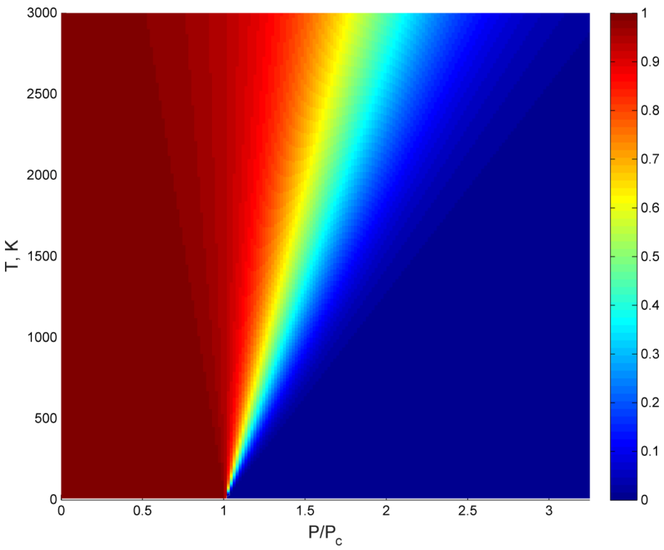


FIG. 1. HS-state population vs pressure and temperature in the absence of the exchange interaction ($J = 0$).

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 $\Delta P_0 \approx 4.2$ GPa and $\Delta P_1 \approx 8.4$ GPa. Note that in the absence of cooperativity ($J = 0$) the 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,

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

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.

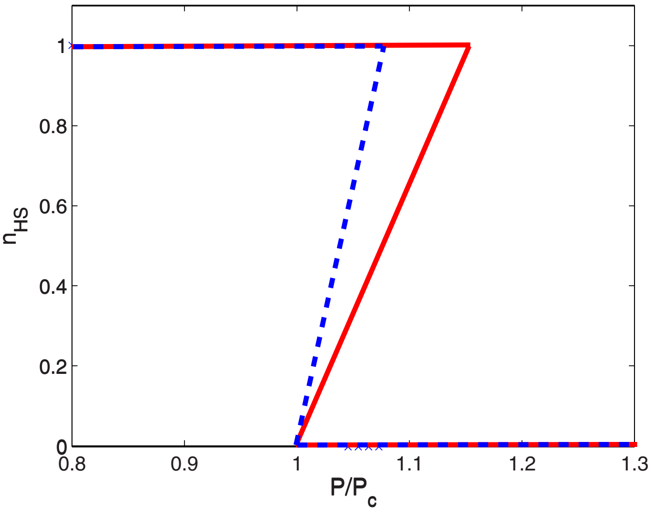


FIG. 2. The HS fraction vs pressure. Red solid line: $T = 0, m = 1$; blue dashed line: $T = 0, m = 0$.

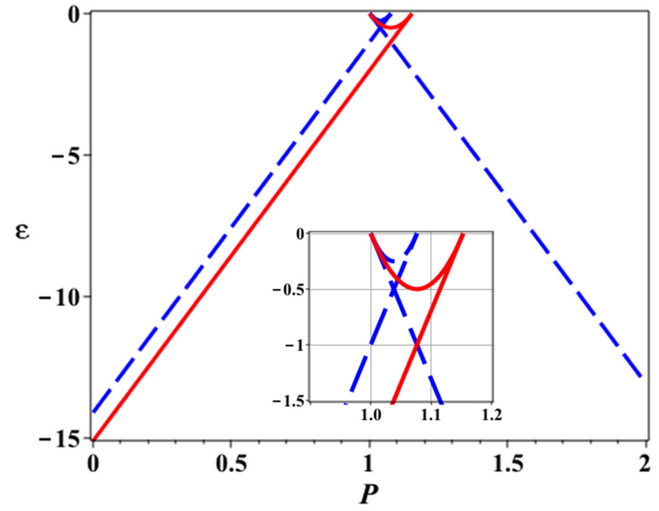


FIG. 3. Energy of the system, $\varepsilon = E/E_0$, at zero temperature vs pressure for $m = 0$ (blue dashed curve) and $m = 1$ (red solid curve).

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

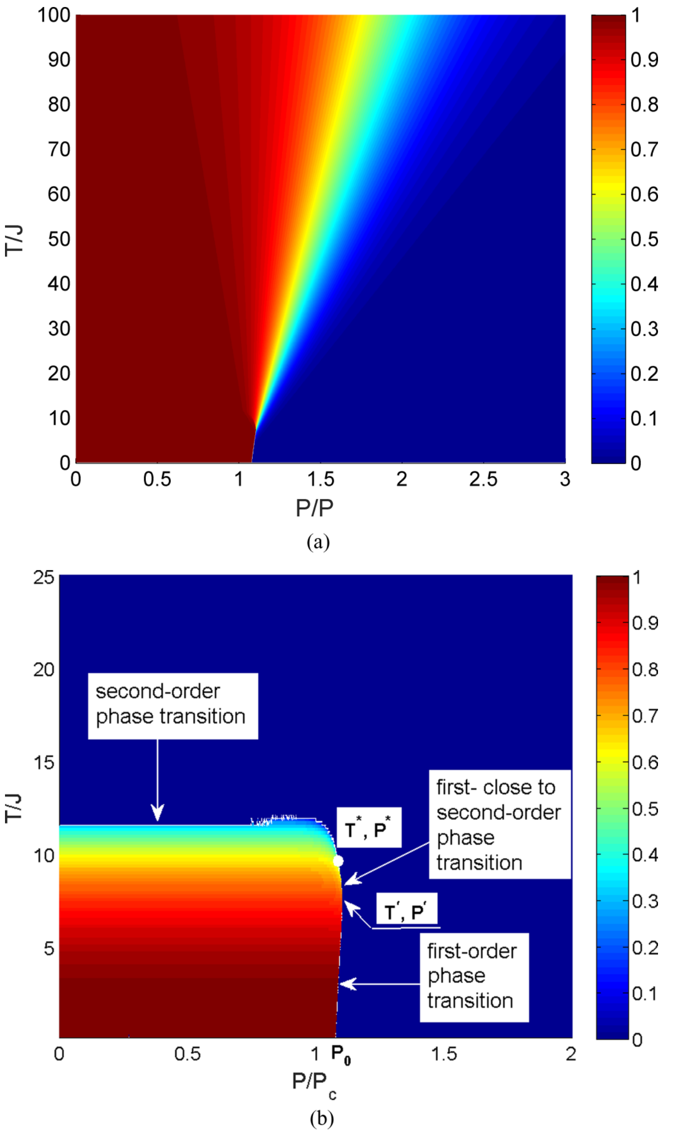
$$H_0 = \frac{\nu m^2}{2} n(3n-1) - \frac{\nu}{2} n(1-n). \tag{31}$$

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

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

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

Figures 4(a) and 4(b) depict P-T phase diagrams of the HS-state population n_{HS} and magnetization m, corresponding to the minimum free energy F (30), respectively.



(a)

(b)

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

In Fig. 5 all the possible self-consistent solutions of the system of equations (22) and (23) for the above set of parameters, marked with red circles for the magnetization m and blue crosses for the population of the HS state n_{HS} for some specific values of external pressure (see below) as a function of temperature, are depicted. Those solutions that correspond to the minimum of the free energy are connected by solid lines (red lines for the magnetization m and blue lines 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 state is a nonmagnetic LS state. The increase in 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 transformed into a nonmagnetic state by the first-order transition. The crossing of two energies that are typical for the first-order phase transitions is clearly visible in Fig. 3. In the range of pressure $P \leqslant P_0$ [Figs. 4(b), 5(a) and 5(b)] with increasing temperature the system undergoes the second-order phase transition to the paramagnetic state. In the P-T diagrams of a physical system (Fig. 4) the existence of a singular point, the so-called tricritical point [T^*, P^* in Fig. 4(b)], at which the second-order phase transition line continuously crosses the line of the first-order phase transitions, is clearly visible. At $P > P_0$ the ground state of the system is not magnetic. With increasing temperature, the magnetic HS state is populated, and due to the first-order phase transition the antiferromagnetic phase is restored [Figs. 5(c) and 5(d)] as it is energetically more favorable for $P \leqslant P'$. 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 a further increase in temperature the system goes into the paramagnetic state via a phase transition of the second order if $P \leqslant P^*$ and of the first

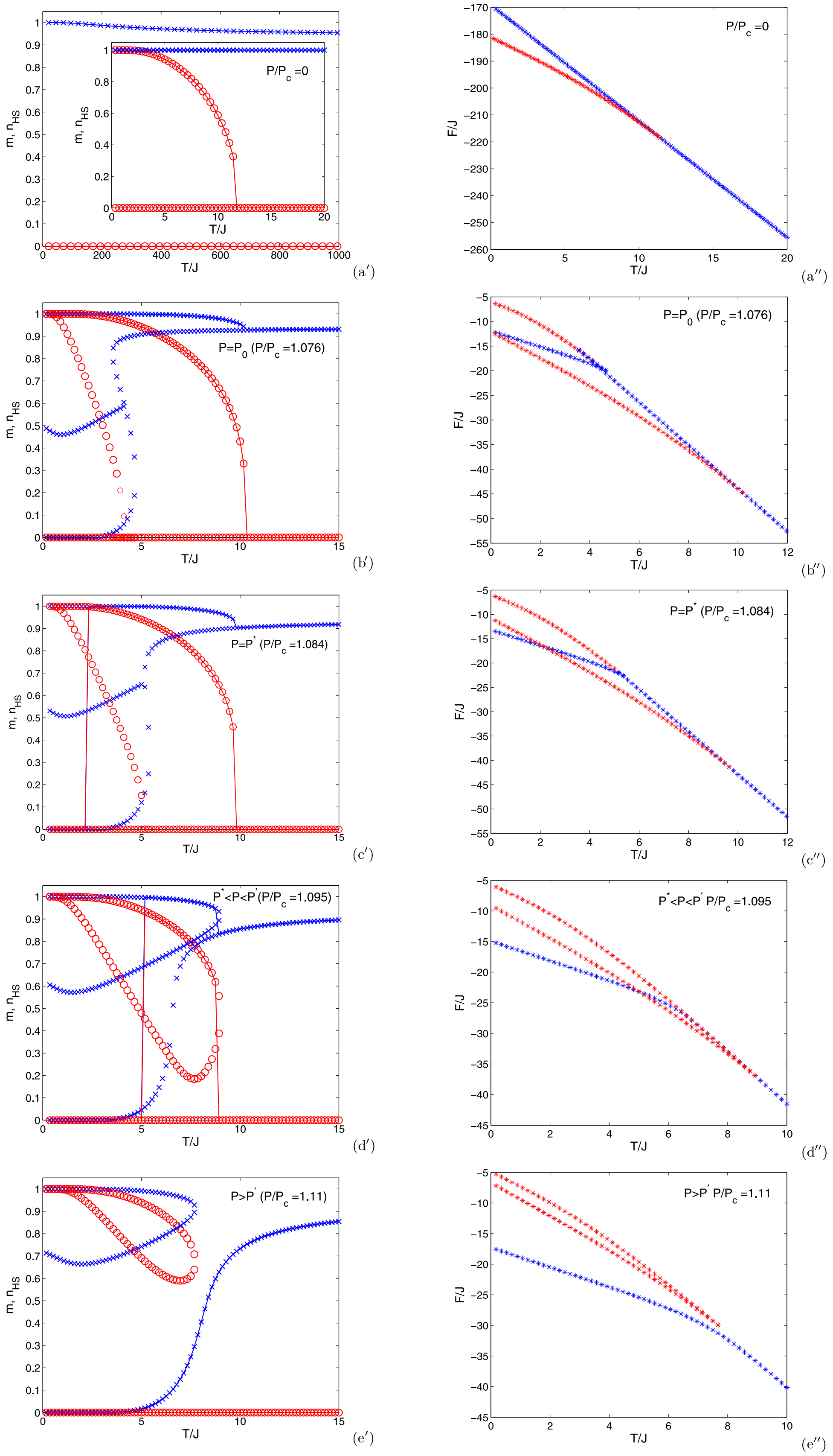


FIG. 5. Solutions of Eqs. (22) and (23) for different values of external pressure as a function of temperature. Pairs of solutions for the magnetization (circles) and the population of the HS state (crosses), for which the thermodynamic potential (right panel) has the lowest value, are connected by a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

order close to the second if $P^* < P \leqslant P'$ [Fig. 5(d)]. With increasing pressure at $P > P_C$ an energy interval between the ground nonmagnetic LS state and the nearest excited magnetic HS state is increased. When $P > P'$ [Fig. 5(e)], the thermal energy required for the HS-state population to reach the desired extent becomes comparable with the value of the exchange interaction J, and magnetic order disappears.

V. CONCLUSION

Previously, the effect of interatomic Coulomb and exchange interaction was studied in Ref. [19], where quite similar mean-field solutions were obtained. We studied the effect of pressure on SCO that was not discussed in [19].

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 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 [71]. 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 reconstructed into a thermodynamic transition of the first and then of the second order. The appearance of first-order phase transitions with discontinuities of the magnitude of the magnetic moment and the population of ionic terms due to the large (up to 10%) difference in the HS and LS ionic radii results in a break in the volume of the crystal as a function of temperature and pressure. Metastable states contribute 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 we obtained 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 message 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 in 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 [72]. Competition and interplay between the short-range and long-range interactions are interesting topics in phase transitions [73–80]. 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 [43]. This effect should be experimentally observable as an absence of critical opalescence [43,79,80]. Phase transitions in such systems belong to the mean-field universality class.

In [81,82] the authors showed short-range interactions favoring nearest-neighbor HS-LS pairs (called antiferromagneticlike) and a long-range (elastic) interaction favoring all molecules in the same spin state (all LS or all HS, called ferromagneticlike). In our work we found 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, an analysis of the SCO system was carried out for a 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 from the general case, which includes the possible change in the system volume, will be only quantitative. In order to take the latter effect into account, one should consider the Gibbs thermodynamic potential instead of the Helmholtz free energy. That research 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 [83]. In the magnetically ordered phase, at $T < T_N$, a sharp volume jump is observed, and at $T > T_N$ only a smooth change occurs, while in most cases the symmetry of the crystal is conserved. So at $T = 300$ K for (MgFe)O and $GdFe_3(BO_3)_4$, for which $T_N < 300$ K, there is a smooth change in volume. For $FeBO_3$ ($T_N = 348$ K) 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 [83].

Summarizing, the main 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 is 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.

ACKNOWLEDGMENTS

The reported study was funded by the Russian Foundation for Basic Research; the government of Krasnoyarsk Territory; the Krasnoyarsk Region Science and Technology

Support Fund for research Projects No. 16-42-243048, No. 16-42-240413, No. 16-42-240746, and No. 16-43-240505; the Council of the President of the Russian Federation for Support of Young Scientists and Leading Scientific Schools, Projects No. SP-1844.2016.1 and No. NSh-7559.2016.2; and the Russian Foundation for Basic Research, Projects No. 16-02-00507, No. 16-02-00098, and No. 16-02-00273. A.I.N. acknowledges the support from CONACyT.

APPENDIX: MEAN-FIELD APPROXIMATION

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

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

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

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 $\langle\cdots\rangle$ denotes the average value. In the mean-field approximation one neglects the contribution of the second-order terms in the fluctuations, so that

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

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

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

In the mean-field approximation the spins and pseudospins are independent of each other, and their 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* [84,85]. 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

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

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 ($\alpha = 2$) fractions. Here and below, for $J_{\alpha\beta}$ and ξ we 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

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

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 neighbors we obtain

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

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:

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

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

---

[1] L. Cambi and A. Cagnasso, Atti Accad. Lincei **13**, 809 (1931).

[2] C. M. Jureschi, J. Linares, A. Rotaru, M. H. Ritti, M. Parlier, M. M. Dîrtu, M. Wolff, and Y. Garcia, Sensors **15**, 2388 (2015).

[3] I. P. Bazarov, *Thermodynamics* (Pergamon, Oxford, 1964).

[4] J. Liu, J.-F. Lin, Z. Mao, and V. B. Prakapenka, Am. Mineral. **99**, 84 (2014).

[5] J. Liu, J.-F. Lin, and V. B. Prakapenka, Sci. Rep. **5**, 7640 (2015).

[6] J. F. Lin, G. Vanko, S. D. Jacobsen, V. Iota-Herbei, V. V. Struzhkin, V. B. Prakapenka, A. Kuznetsov, and C. S. Yoo, Science **317**, 1740 (2007).

[7] I. S. Lyubutin, V. V. Struzhkin, A. A. Mironovich, A. G. Gavriliuk, P. G. Naumov, J.-F. Lin, Sergey G. Ovchinnikov, S. Sinogeikin, P. Chow, Y. Xiao, and R. J. Hemley, Proc. Natl. Acad. Sci. USA **110**, 7142 (2013).

[8] S. G. Ovchinnikov, T. M. Ovchinnikova, P. G. Dyad'kov, V. V. Plotkin, and K. D. Litasov, JETP Lett. **96**, 129 (2012).

[9] D. Chernyshov, H.-B. Burgi, M. Hostettler, and K. W. Tornroos, Phys. Rev. B **70**, 094116 (2004).

[10] J. Wajnsflasz and R. Pick, J. Phys. Colloq. **32**, 1 (1971).

[11] R. A. Bari and J. Sivardidre, Phys. Rev. B **5**, 4466 (1972).

[12] J. Linares, H. Spiering, and F. Varret, Eur. Phys. J. B **10**, 271 (1999).
[13] M. M. Dîrtu, Y. Garcia, M. Nica, A. Rotaru, J. Linares, and F. Varret, Polyhedron **26**, 2259 (2007).
[14] A. B. Koudryavtsev and W. Linert, J. Struct. Chem. **50**, 1181 (2009).
[15] J. Wajnflasz, Phys. Status Solidi **40**, 537 (1970).
[16] A. Bousseksou, H. Constant-Machado, and F. Varret, J. Phys. I **5**, 747 (1995).
[17] M. Nishino, K. Boukheddaden, S. Miyashita, and F. Varret, Phys. Rev. B **68**, 224402 (2003).
[18] S. Miyashita, Y. Konishi, H. Tokoro, M. Nishino, K. Boukheddaden, and F. Varret, Prog. Theor. Phys. **114**, 719 (2005).
[19] Y. Konishi, H. Tokoro, M. Nishino, and S. Miyashita, J. Phys. Soc. Jpn. **75**, 114603 (2006).
[20] A. Dobrinescu, C. Enachescu, and A. Stancu, J. Magn. Magn. Mater. **321**, 4132 (2009).
[21] H. Banerjee, M. Kumar, and T. Saha-Dasgupta, Phys. Rev. B **90**, 174433 (2014).
[22] K. Boukheddaden, I. Shteto, B. Hôo, and F. Varret, Phys. Rev. B **62**, 14796 (2000).
[23] K. Boukheddaden, I. Shteto, B. Horomano, and F. Varret, Phys. Rev. B **62**, 14806 (2000).
[24] F. Varret, S. A. Salunke, K. Boukheddaden, A. Bousseksou, E. Codjovi, C. Enachescu, and J. Linares, C. R. Chim. **6**, 385 (2003).
[25] M. Nishino, S. Miyashita, and K. Boukheddaden, J. Chem. Phys. **118**, 4594 (2003).
[26] K. Boukheddaden, J. Linares, E. Codjovi, F. Varret, V. Niel, and J. A. Real, J. Appl. Phys. **93**, 7103 (2003).
[27] K. Boukheddaden, J. Linares, R. Tanasa, and C. Chong, J. Phys. Condens. Matter **19**, 106201 (2007).
[28] S. Mouri, K. Tanaka, S. Bonhommeau, N. O. Moussa, G. Molnar, and A. Bousseksou, Phys. Rev. B **78**, 174308 (2008).
[29] A. Atitoaie, R. Tanasa, and C. Enachescu, J. Magn. Magn. Mater. **324**, 1596 (2012).
[30] D. Chiruta, J. Linares, P. R. Dahoo, and M. Dimian, Phys. B (Amsterdam, Neth.) **435**, 76 (2014).
[31] I. Gudyma, A. Maksymov, and C. Enachescu, Phys. Rev. B **89**, 224412 (2014).
[32] I. Gudyma, A. Maksymov, and M. Dimian, Phys. Rev. E **90**, 052135 (2014).
[33] M. Paez-Espejo, M. Sy, F. Varret, and K. Boukheddaden, Phys. Rev. B **89**, 024306 (2014).
[34] W. Laosiritaworn and Y. Laosiritaworn, Polyhedron **66**, 108 (2013).
[35] T. Kambara, J. Phys. Soc. Jpn. **50**, 2257 (1981).
[36] V. V. Shelest, A. V. Hristov, and G. G. Levchenko, Fiz. Nizk. Temp. **42**, 644 (2016).
[37] G. G. Levchenko, A. V. Hristov, and V. N. Varyuhin, Fiz. Nizk. Temp. **40**, 737 (2014).
[38] C. Timm and C. J. Pye, Phys. Rev. B **77**, 214437 (2008).
[39] A. Marbeuf, S. F. Matar, P. Negrier, L. Kabalan, J.-F. Letard, and P. Guionneau, Chem. Phys. **420**, 25 (2013).
[40] M. Nishino, K. Boukheddaden, Y. Konishi, and S. Miyashita, Phys. Rev. Lett. **98**, 247203 (2007).
[41] K. Boukheddaden, M. Nishino, and S. Miyashita, Phys. Rev. Lett. **100**, 177206 (2008).
[42] Y. Konishi, H. Tokoro, M. Nishino, and S. Miyashita, Phys. Rev. Lett. **100**, 067206 (2008).
[43] S. Miyashita, Y. Konishi, M. Nishino, H. Tokoro, and P. A. Rikvold, Phys. Rev. B **77**, 014105 (2008).
[44] A. Bousseksou, G. Molnar, J.-P.Tuchagues, N. Menendez, E. Codjovi, and F. Varret, C. R. Chim. **6**, 329 (2003).
[45] A. O. Sboychakov, K. I. Kugel, A. L. Rakhmanov, and D. I. Khomskii, Phys. Rev. B **80**, 024423 (2009).
[46] S. G. Ovchinnikov, V. A. Gavrichkov, M. M. Korshunov, and E. I. Shneyder, in *Theoretical Methods for Strongly Correlated Systems*, edited by A. Avella and F. Mancini, Springer Series in Solid-State Sciences Vol. 171 (Springer, Berlin, 2012), pp. 143–171.
[47] C. M. Varma, S. Schmitt-Rink, and A. E. Ruckenstein, Solid State Commun. **62**, 681 (1987).
[48] V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987).
[49] Y. B. Gaididei and V. M. Loktev, Phys. Status Solidi B **147**, 307 (1988).
[50] S. G. Ovchinnikov, Phys. Usp. **40**, 993 (1997).
[51] S. G. Ovchinnikov and Y. S. Orlov, J. Exp. Theor. Phys. **104**, 436 (2007).
[52] Y. Tanabe and S. Sugano, J. Phys. Soc. Jpn. **9**, 753 (1954).
[53] J. Hubbard, Proc. R. Soc. London, Ser. A **277**, 237 (1964).
[54] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).
[55] L. F. Feiner, J. H. Jefferson, and R. Raimondi, Phys. Rev. B **53**, 8751 (1996); **53**, 8774 (1996).
[56] K. A. Chao, J. Spalek, and A. M. Oles, J. Phys. C **10**, L271 (1977).
[57] V. A. Gavrichkov, S. I. Polukeev, and S. G. Ovchinnikov, Phys. Rev. B **95**, 144424 (2017).
[58] K. I. Kugel' and D. I. Khomskii, Sov. Phys. Usp. **25**, 231 (1982).
[59] G. D' Avino and A. Painelli, Phys. Rev. B **84**, 104119 (2011).
[60] S. Decurtins, P. Guetlich, C. P. Koehler *et al.*, Chem. Phys. Lett. **105**, 1 (1984).
[61] S. G. Ovchinnikov, J. Exp. Theor. Phys. **107**, 140 (2008).
[62] S. G. Ovchinnikov, J. Phys. Condens. Matter **17**, S743 (2005).
[63] S. G. Ovchinnikov, J. Exp. Theor. Phys. **116**, 123 (2013).
[64] K. A. Lobach, S. G. Ovchinnikov, and T. M. Ovchinnikova, J. Exp. Theor. Phys. **120**, 132 (2015).
[65] Z. Wu, J. F. Justo, C. R. S. da Silva, S. de Gironcoli, and R. M. Wentzcovitch, Phys. Rev. B **80**, 014409 (2009).
[66] J.-F. Lin, A. G. Gavriliuk, V. V. Struzhkin, S. D. Jacobsen, W. Sturhahn, M. Y. Hu, P. Chow, and C.-S. Yoo, Phys. Rev. B **73**, 113107 (2006).
[67] J.-F. Lin, V. V. Struzhkin, A. G. Gavriliuk, and I. Lyubutin, Phys. Rev. B **75**, 177102 (2007).
[68] I. S. Lyubutin, A. G. Gavriliuk, K. V. Frolov, J. F. Lin, and I. A. Troyan, JETP Lett. **90**, 617 (2009).
[69] W. Sturhahn, J. M. Jackson, and J. -F. Lin, Geophys. Res. Lett. **32**, L12307 (2005).
[70] T. Tsuchiya, R. M. Wentzcovitch, C. R. S. da Silva, and S. de Gironcoli, Phys. Rev. Lett. **96**, 198501 (2006).
[71] A. I. Nesterov and S. G. Ovchinnikov, JETP Lett. **90**, 530 (2009).
[72] W. Nicolazzi, S. Pillet, and C. Lecomte, Phys. Rev. B **78**, 174401 (2008).
[73] B. Pluis, T. N. Taylor, D. Frenkel, and J. F. van der Veen, Phys. Rev. B **40**, 1353 (1989).
[74] U. Low, V. J. Emery, K. Fabricius, and S. A. Kivelson, Phys. Rev. Lett. **72**, 1918 (1994).
[75] C. Sagui and R. C. Desai, Phys. Rev. E **49**, 2225 (1994).
[76] C. B. Muratov, Phys. Rev. E **66**, 066108 (2002).

[77] F. Sciortino, S. Mossa, E. Zaccarelli, and P. Tartaglia, Phys. Rev. Lett. **93**, 055701 (2004).

[78] A. Giuliani, J. L. Lebowitz, and E. H. Lieb, Phys. Rev. B **74**, 064420 (2006).

[79] T. Nakada, P. A. Rikvold, T. Mori, M. Nishino, and S. Miyashita, Phys. Rev. B **84**, 054433 (2011).

[80] T. Nakada, T. Mori, S. Miyashita, M. Nishino, S. Todo, W. Nicolazzi, and P. A. Rikvold, Phys. Rev. B **85**, 054408 (2012).

[81] M. Nishino and S. Miyashita, Phys. Rev. B **88**, 014108 (2013).

[82] P. A. Rikvold, G. Brown, S. Miyashita, C. Omand, and M. Nishino, Phys. Rev. B **93**, 064109 (2016).

[83] I. S. Lyubutin and A. G. Gavriliuk, Phys. Usp. **52**, 989 (2009).

[84] G. W. Pratt, Jr., Phys. Rev. **106**, 53 (1957).

[85] G.W. Pratt, Jr., Phys. Rev. **108**, 1233 (1957).