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ORDER, DISORDER, AND PHASE TRANSITION IN CONDENSED SYSTEM

Superexchange Interaction in Magnetic Insulators with Spin Crossover

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Abstract—We present the derivation of a microscopic superexchange Hamiltonian for undoped magnetic insulators with an arbitrary spin. It is established that the sign of the (ferromagnetic or antiferromagnetic) superexchange between magnetic ions in the d^n configuration depends on the spin nature of virtual multielectron states $d^{n\pm1}$, viz., low-spin or high-spin partners with $S \pm 1/2$ relative to ground state of the d^n configuration with spin S. A macroscopic substantiation is given for the Goodenough–Kanamori rules and simple mean-field estimates connecting the magnetic ordering temperature with the exchange constant. The conventional Anderson superexchange for magnetic materials with spin $S = 1/2$ and the P/T magnetic phase diagram for ferroborate $FeBO_3$ with spin crossover $S = (5/2 \leftrightarrow 1/2)$ at the Fe^{3+} ion under a high pressure are also reproduced as a test.

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1. INTRODUCTION

It is well known that phase transitions with spin crossover at a magnetic ion can be induced by an external pressure [1]. Analysis of the evolution of the magnetic order in the spin crossover conditions is usually based on the concepts borrowed from the Hubbard model [2, 3], in which the effective Heisenberg-type exchange Hamiltonian with exchange parameter $J = t^2/U$ (t is the hopping integral and U is the Coulomb interaction potential at an atom) preserves its form for all values of pressure, and the spin of a cation changes its value at the crossover point. Such a simplified approach is justified at the first stage of the research, when the initial idea concerning the interrelation between the electronic structure and the superexchange interaction under the external action are formulated. It should be noted that analogous changes in the spin value can be induced by an optical excitation [4, 5] at the frequency of the d–d transition. Later, a microscopic approach accounting for the effects of pressure [6] as well as optical pumping [7] on the electronic structure and the superexchange interaction in the Mott–Hubbard materials was developed. The aspects associated with structural effects in the spin crossover have also been investigated recently in [8], where the physical origin of these effects was attributed to the difference in the ionic radii of the competing states with different spins. However, the thermodynamic relations in [8] contain the superexchange interaction that has been introduced phenomenologically, and its behavior during the crossover remains unclear. A consistent approach to the description of the exchange interaction between ions with possible coexistence of different multielectron terms requires separate accurate analysis because only the ground terms of the involved multielectron states of ions participate in the standard theory of exchange interaction. Precisely this problem is considered in this article. It should be noted that an analogous problem was considered earlier in [9, 10]. In the course of our analysis, we will compare, whenever possible, our results with the conclusion drawn in [9, 10] concerning the superexchange. In spite of the fact that the formulation of the problem in [9, 10] differs from that in the present work, our approach is methodically similar. In particular, the multielectron representation using the Hubbard X operators is used in both cases.

We are also interested in the correctness of simple physical estimates in analysis of spin crossovers and the situation in which the corresponding inaccuracies the derivation of microscopic parameters for specific materials are immaterial. By way of example, we will use iron borate $FeBO_3$ with a high spin $S = 5/2$ in the undeformed state [3]. Since the initial local density approximation and the generalized tight binding (LDA + GTB) approach has been discussed more than once (see, for example, [11, 12]), the emphasis in our study will be laid precisely on the theory of superexchange in magnetic insulators, which will be constructed in the second order of perturbation theory from the GTB Hamiltonian.

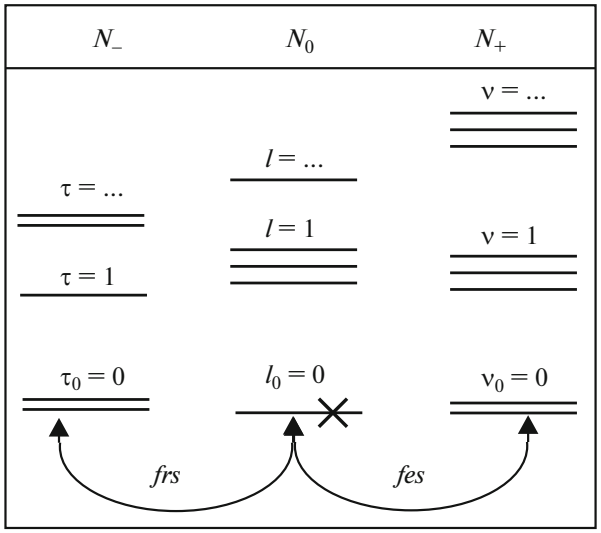

Fig. 1. Configuration space of a unit cell of a Mott–Hubbard material. The cross on the ground energy level for the configuration with N_0 electrons indicates the state occupied at zero temperature; all remaining states are empty. Arrows indicate quasiparticle states with the lowest binding energy (first removal electron states (*frs*), viz., a hole at the top of the valence band and first extra states (*fes*), viz., an electron at the bottom of the conduction band [24]).

2. SUPEREXCHANGE INTERACTION OF MAGNETIC IONS WITH AN ARBITRARY SPIN

There are many approaches to analysis of the superexchange interaction in the Hubbard model and its multiband generalizations (see [13–21] and the literature cited therein). In addition, a consistent approach using the X operators was developed in [9, 10]. Only the contributions of the ground terms of the multielectron states are often taken into account, viz., the filled d^n term and unfilled $d^{(n-1)}$ and $d^{(n+1)}$ terms, which will be referred to as virtual states. In the case of spin crossover, the states of high-spin as wells low-spin terms must be taken into account simultaneously in each of the configuration d^n, $d^{(n-1)}$, and $d^{(n+1)}$ of the magnetic ion. We will operate from the very outset within the cell perturbation method in constructing the effective Hamiltonian, which is logically matched with the LDA + GTB approach to calculating the electronic structure [12], as well as the superexchange approximation in Mott–Hubbard materials under an external action [6, 7]. We begin with the multielectron Hamiltonian in the representation of X operators, $\hat{H} = \hat{H}_0 + \hat{H}_1$, where

$$\hat{H}_0 = \sum_f \Bigg\{ \sum_\tau (\varepsilon_\tau - N_-\mu) X_f^{\tau\tau} + \sum_l (\varepsilon_l - N_0\mu) X_f^{ll} + \sum_\nu (\varepsilon_\nu - N_+\mu) X_f^{\nu\nu} \Bigg\}, \quad (1)$$

$$\hat{H}_1 = \sum_{fg} \sum_{rr'} t_{fg}^{rr'} X_f^{r+} X_g^{r'}, \quad (2)$$

as well as

$$t_{fg}^{rr'} = \sum_{\lambda\lambda'} \sum_\sigma t_{fg}^{\lambda\lambda'} [\gamma^*_{\lambda\sigma}(r)\gamma_{\lambda'\sigma}(r') + \gamma^*_{\lambda'\sigma}(r)\gamma_{\lambda\sigma}(r')] \quad (3)$$

and

$$\gamma_{\lambda\sigma}(r) = \langle (N_+, M_S)_\nu | d(p)^+_{\lambda f\sigma} | (N_0, M_S)_l \rangle \times \delta(S_\nu, S_l \pm |\sigma|) \delta(M_\nu, M_l + \sigma), \quad (4)$$

here, root vectors r and r' run through all possible one-particle transitions $\{l, \nu\}$ (creation of an electron) and $\{l, \tau\}$ (creation of a hole) between the multielectron states

$$|l\rangle = |(N_0, M_S)_l\rangle \quad \text{and} \quad |\nu(\tau)\rangle = |(N_\pm, M_S)_{\nu(\tau)}\rangle$$

with energies ε_l and $\varepsilon_{\nu(\tau)}$ in the sectors of the configuration space in Fig. 1 with N_0 and $N_\pm = N_0 \pm 1$ electrons per cell.

The derivation of this Hamiltonian from the Hamiltonian $\hat{H} = \hat{H}_d + \hat{H}_p + \hat{H}_{pd} + \hat{H}_{pp}$ of the *pd* model, where

$$\hat{H}_d = \sum_{\lambda f\sigma} \Bigg[(\varepsilon_\lambda - \mu) d^+_{\lambda f\sigma} d_{\lambda f\sigma} + \frac{1}{2} U_\lambda n^\sigma_{\lambda f} n^{\bar\sigma}_{\lambda f} + \sum_{\lambda'\sigma'} \Bigg(-J_{\lambda\lambda'} d^+_{\lambda f\sigma} d_{\lambda\bar\sigma} d^+_{\lambda' f\bar\sigma} d_{\lambda' f\sigma} + \sum_{f'} V_{\lambda\lambda'} n^\sigma_{\lambda f} n^{\sigma'}_{\lambda' f'} \Bigg) \Bigg],$$

$$\hat{H}_p = \sum_{\lambda f\sigma} \Bigg[(\varepsilon_{p\lambda} - \mu) p^+_{\lambda f\sigma} p_{\lambda f\sigma} + \frac{1}{2} U^p_\lambda n^{p\sigma}_{\lambda f} n^{p\bar\sigma}_{\lambda f} + \sum_{\lambda' g\sigma'} V^p_{\lambda\lambda'} n^{p\sigma}_{\lambda f} n^{p\sigma'}_{\lambda' g} \Bigg], \quad (5)$$

$$\hat{H}_{pd} = \sum_{fg} \sum_{\lambda\lambda'\sigma\sigma'} (t_{fg}^{\lambda\lambda'} p^+_{\lambda f\sigma} d_{\lambda' d\sigma} + \text{H.c.} + V_{\lambda\lambda'} n^{p\sigma}_{\lambda f} n^{\sigma'}_{\lambda' g}),$$

$$\hat{H}_{pp} = \sum_{fg} \sum_{\lambda\lambda'\sigma} (t_{pfg}^{\lambda\lambda'} p^+_{\lambda f\sigma} p_{\lambda' g\sigma} + \text{H.c.})$$

has already been considered in [11, 22]. Here, $n^\sigma_{\lambda f} = d^+_{\lambda f\sigma} d_{\lambda f\sigma}$, $n^{p\sigma}_{\lambda f} = p^+_{\lambda f\sigma} p_{\lambda f\sigma}$, and subscripts f and g run through all cells with localized atomic ($d_{\lambda f}$) and cellular ($p_{\lambda f}$) orbitals with energies ε_λ and $\varepsilon_{p\lambda}$; $t_{fg}^{\lambda\lambda'}$ and $t_{pfg}^{\lambda\lambda'}$ are the matrix elements of the *pd* and *pp* jumps; U_λ, U^p_λ, and $J_{\lambda\lambda'}$ are the Coulomb interaction potentials at an orbital and the Hund exchange interaction; $V_{\lambda\lambda'}$ is the electron repulsion energy at the cation of a transition element and at the oxygen atom, and subscript λ runs through all irreducible representations of the symmetry group of a cell. In accordance with the general procedure of a transition to the multielectron rep-

resentation, one-electron $p^+_{\lambda f\sigma}$ and $d^+_{\lambda f\sigma}$ operators can be written in the form of a superposition of transitions involving low- and high-spin partners $|\nu(\tau)\rangle$ with $S_{\nu(\tau)} = S_l \pm 1/2$ relative to the ground state $|l\rangle$:

$$d^+_{\lambda f\sigma} = \sum_{l\nu}[\gamma^{(t)}_\lambda(l\nu)\alpha^{(t)+}_{f\sigma}(\nu l) + \gamma^{(s)}_\lambda(l\nu)\alpha^{(s)+}_{f\sigma}(\nu l)] + \sum_{\tau l}[\gamma^{(t)}_\lambda(l\tau)\beta^{(t)+}_{f\sigma}(\tau l) + \gamma^{(s)}_\lambda(\tau l)\beta^{(s)+}_{f\sigma}(l\tau)], \quad (6)$$

where new operators $\alpha^{(s,t)+}_{f\sigma}(\nu l)$ and $\beta^{(s,t)+}_{f\sigma}(l\tau)$ are given in accordance with the momenta summation rules by

$$\alpha^{(s)+}_{f\sigma}(\nu l) = \eta(\sigma)\sum_{-M_\nu}^{M_\nu}\sqrt{\frac{S_l - \eta(\sigma)M_\nu + 1/2}{2S_l+1}}X_f^{M\nu, M_l = M_\nu - \sigma},$$

$$\beta^{(t)+}_{f\sigma}(l\tau) = \sum_{-M_l}^{M_l}\sqrt{\frac{S_\tau + \eta(\sigma)M_l + 1/2}{2S_\tau+1}}X_f^{Ml, M_\tau = M_l - \sigma},$$

$$\alpha^{(t)+}_{f\sigma}(\nu l) = \sum_{-M_\nu}^{M_\nu}\sqrt{\frac{S_l + \eta(\sigma)M_\nu + 1/2}{2S_l+1}}X_f^{M\nu, M_l = M_\nu - \sigma}, \quad (7)$$

$$\beta^{(s)+}_{f\sigma}(\tau l) = \eta(\sigma)\sum_{-M_l}^{M_l}\sqrt{\frac{S_\tau - \eta(\sigma)M_l + 1/2}{2S_\tau+1}}X_f^{Ml, M_\tau = M_l - \sigma}.$$

Operator $\alpha^{(s,t)+}_{i\sigma}$ corresponds to the quasiparticle excitation of electrons in the valence band, $N_-(S_\tau) \to N_0(S_l = S_\tau - 1/2)$ with a decrease of spin by 1/2 and $N_-(S_\tau) \to N_0(S_l = S_\tau + 1/2)$ with an increase of spin by 1/2 for s and t indices, respectively. Analogous expressions can be written for $\beta^{(s,t)+}_{i\sigma}$ with the substitutions $\tau \leftrightarrow l$ and $l \leftrightarrow \nu$ in the conduction band. Actually, the main criterion in the transition from Hamiltonian (5) to (1) and (2) is the possibility of constructing well-localized Wannier functions for the X operators, while the disadvantage is the lack of a general derivation of the representation for "canonical fermions" [23] or an analogous representation of a more general form [11, 22, 25, 26] for an arbitrary symmetry of the cell. We will further assume that such a representation still exists, and the Wannier functions for a cell are localized sufficiently for disregarding the contributions of the Coulomb interaction between electrons in different cells. In such an approach, quasiparticles are one-electron excitations on the basis of multielectron states of a cell, which correspond to transitions between different sectors N_0 and $N_\pm$ of the configuration space. Each such excitation forms a quasiparticle band with root vector r in the configuration space for all possible $|l\rangle$, $|\nu\rangle$, and $|\tau\rangle$ multielectron states of the cell (see Fig. 1). The superexchange interaction $\hat{H}_1$ appears in the second order of perturbation theory relative to hopping processes, which corresponds to virtual perturbations via the dielectric gap to the conduction band and back. These excitations are described by nondiagonal elements $t^{rr'}_{fg}$ with root vectors $r = \{\tau, l\}$ and $\{l, \nu\}$. In the Hubbard model, there is only one such element corresponding to excitations between the lower and upper Hubbard bands. In the general case, as can be seen from Fig. 1, the number of such contributions can be significant. For separating these contributions, we can use the method of projection operator P_τ and P_ν [13] for a Mott–Hubbard material with an arbitrary spectrum [7], where

$$P_\tau = \left(X_i^{\tau\tau} + \sum_l X_i^{l,l}\right)\left(X_j^{\tau\tau} + \sum_{l'} X_j^{l',l'}\right),$$

$$P_\nu = X_i^{\nu,\nu} + X_j^{\nu,\nu} - X_i^{\nu,\nu}\sum_{\nu'} X_j^{\nu',\nu'}, \quad 1 \le \tau \le N_\tau,$$

$$1 \le l \le N_l, \quad 1 \le \nu \le N_\nu.$$

Each of these operators satisfies the relations

$$\left(\sum_{\tau=1}^{N\tau} P_\tau + \sum_{\nu=1}^{N\nu} P_\nu\right) = 1,$$

$$P_\tau P_\nu = 0, \quad P_\tau P_{\tau'} = \delta_{\tau\tau'}P_\tau, \quad P_\nu P_{\nu'} = \delta_{\nu\nu'}P_\nu.$$

Let us introduce the Hamiltonian of the exchange-coupled (i, j) pair:

$$\hat{h}_{ij} = (\hat{h}_0 + \hat{h}_1^{\text{in}}) + \hat{h}_1^{\text{out}},$$

where

$$(\hat{h}_0 + \hat{h}_1^{\text{in}}) = \sum_{\tau\tau'} P_\tau \hat{h} P_{\tau'} + \sum_{\nu\nu'} P_\nu \hat{h} P_{\nu'},$$

$$\hat{h}_1^{\text{out}} = \left(\sum_\tau P_\tau\right)\hat{h}\left(\sum_\nu P_\nu\right) + \left(\sum_\nu P_\nu\right)\hat{h}\left(\sum_\tau P_\tau\right)$$

are the intra- and interband contributions for

$$\hat{H} = \sum_{ij}\hat{h}_{ij}.$$

In the unitary transformation of the Hamiltonian of the (i, j) pair, we have $\tilde{h} = e^{\hat{G}}\hat{h}_{ij}e^{-\hat{G}}$, where $\hat{G}$ satisfies the equation

$$\left(\sum_\tau P_\tau\right)\hat{h}_{ij}\left(\sum_\nu P_\nu\right) + \left(\sum_\nu P_\nu\right)\hat{h}_{ij}\left(\sum_\tau P_\tau\right) + \left[\hat{G}, \left(\sum_{\tau\tau'} P_\tau \hat{h}_{ij} P_\tau + \sum_{\nu\nu'} P_\nu \hat{h}_{ij} P_{\nu'}\right)\right]_- = 0, \quad (8)$$

and the transformed Hamiltonian $\hat{h}_1^{\text{out}}$ after the exclusion of interband hops in the second order of pertur-

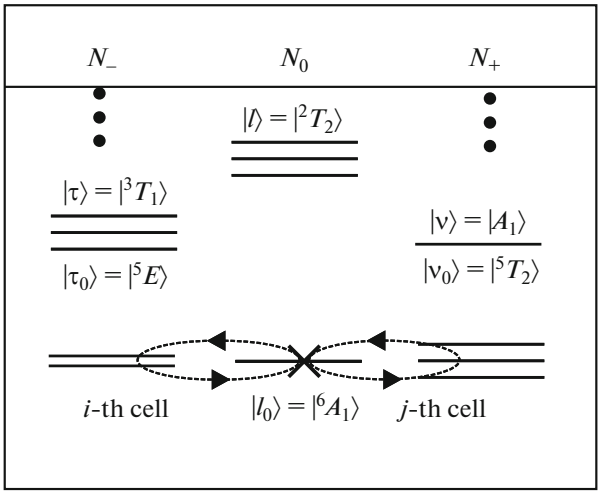

Fig. 2. Configuration space of a unit cell for $FeBO_3$. Ellipses show one-electron transitions involving virtual states $|\tau\rangle$ and $|\nu\rangle$ in the superexchange AFM interaction between the ith and jth cells.

bation theory in interband transitions is given by

$$\tilde{h}_{ij} \approx \left(\sum_{\tau\tau'} P_\tau \hat{h}_{ij} P_{\tau'} + \sum_{\nu\nu'} P_\nu \hat{h}_{ij} P_{\nu'}\right) + \frac{1}{2}\left[G, \left\{\left(\sum_\tau P_\tau\right)\hat{h}_{ij}\left(\sum_\nu P_\nu\right) + \left(\sum_\nu P_\nu\right)\hat{h}_{ij}\left(\sum_\tau P_\tau\right)\right\}\right]_-. \quad (9)$$

Further, we take advantage of the fact that quantities $t_{fg}^{rr'}$ in expression (2) depend on the transitions between spin multiplet components only in terms of the products of the Clebsch–Gordon coefficients in definition (7) for operators $\alpha_{f\sigma}^{(s,t)}$ and $\beta_{f\sigma}^{(s,t)}$ and write $\hat{h}_1^{\text{out}}$ in the equivalent form

$$\hat{h}_1^{\text{out}} = \sum_{l\sigma k}\sum_{\tau\nu k'} t_{ij}^{\nu l,\tau l}\alpha_{i\sigma}^{(k)+}(\nu l)\beta_{j\sigma}^{(k')}(\tau l) + \text{H.c.}, \quad (10)$$

where summation is presumed only over orbital terms $|l\rangle$ and $|\nu\rangle$, $|\tau\rangle$ split into the subsets of low- and high-spin partners, and indices k and k' run through the t- and s-types of quasiparticles. Then hopping integral $t_{fg}^{rr'}$ in expression (10) does not depend on spin variables any longer, and the commutator in expression (9) contains the following quantities:

$$\left(\sum_\tau P_\tau\right)\hat{h}\left(\sum_\nu P_\nu\right) = \sum_{l\sigma k}\sum_{\tau\nu k'} t_{ij}^{\nu l,\tau l}\alpha_{i\sigma}^{(k)+}(\nu l)\beta_{j\sigma}^{(k')}(\tau l),$$
$$\left(\sum_\nu P_\nu\right)\hat{h}\left(\sum_\tau P_\tau\right) = \sum_{l\sigma k}\sum_{\tau\nu k'} t_{ij}^{l\tau,l\nu}\beta_{i\sigma}^{(k)+}(l\tau)\alpha_{j\sigma}^{(k')}(l\nu). \quad (11)$$

In this case, we have

$$\hat{G} = \sum_{l\tau\nu}\left[\frac{t_{ij}^{\nu l,\tau l}}{\Delta_{l\tau\nu}}\sum_{\sigma kk'}\alpha_{i\sigma}^{(k)+}(\nu l)\beta_{j\sigma}^{(k')}(\tau l) - \frac{t_{ij}^{l\tau,l\nu}}{\Delta_{l\tau\nu}}\sum_{\sigma kk'}\beta_{i\sigma}^{(k)+}(l\tau)\alpha_{j\sigma}^{(k')}(l\nu)\right], \quad (12)$$

where $\Delta_{l\tau\nu} = (\varepsilon_\nu + \varepsilon_\tau) - 2\varepsilon_l$ is the energy of production of an electron–hole pair from initial state $|l\rangle$ to final states $|\tau\rangle$ and $|\nu\rangle$; this energy is an analog of the Hubbard repulsion in the simple Hubbard model. We will further operate with spin $S_l = 5/2$ and with the configuration space of iron borate $FeBO_3$ in Fig. 2 [27]. In sector N_-, subscript τ runs through the states

$$|(N_-, M_2)_{\tau_0}\rangle = |^5E\rangle \equiv |t_{2g\uparrow}^3, e_{g\uparrow}^1, L = 1/2\rangle,$$
$$|(N_-, M_1)_{\tau_1}\rangle = |^3T_1\rangle \equiv |t_{2g\uparrow}^3, t_{2g\downarrow}^1, L = 1\rangle \text{ etc.};$$

in sector N_0, subscript l runs through the states

$$|(N_0, M_{5/2})_{l_0}\rangle = |^6A_1\rangle \equiv |t_{2g\uparrow}^3, e_{g\uparrow}^2, L = 0\rangle,$$
$$|(N_0, M_{1/2})_{l_1}\rangle = |^2T_2\rangle \equiv |t_{2g\uparrow}^3, t_{2g\downarrow}^2, L = 1\rangle \text{ etc.};$$

while in sector N_+, subscript ν runs through the states

$$|(N_+, M_2)_{\nu_0}\rangle = |^5T_2\rangle \equiv |t_{2g\uparrow}^3, e_{g\uparrow}^2, t_{2g\downarrow}^1, L = 1\rangle,$$
$$|(N_+, M_0)_{\nu_1}\rangle = |A_1\rangle \equiv |t_{2g\uparrow}^3, t_{2g\downarrow}^3, L = 0\rangle \text{ etc.}$$

This is done to reflect the physical specific features of a given material and to draw conclusions. The superexchange interaction appears even in the second-order of perturbation theory; the effects of the ligand surroundings of magnetic ions are accounted for using the Wannier cell functions and the exact diagonalization procedure in the construction of the configuration space of a unit cell.

To single out spin variables $\hat{S}_l$, as well as $\hat{S}_\nu$ and $\hat{S}_\tau$ in expression (9) in explicit form, we must use their relation with one-particle operators $\alpha_{i\sigma}^{(k)}$ and $\beta_{i\sigma}^{(k)}$ in definition (6); in the unified X representation for these variables and the ground filled high-spin d^5 energy level, these relations have the form

$$\hat{n}_{l\sigma} = (2S_\tau + 1)\beta_\sigma^{(t)+}(l\tau)\beta_\sigma^{(t)}(\tau l) = (2S_l + 1)\alpha_{\bar{\sigma}}^{(s)}(l\nu)\alpha_{\bar{\sigma}}^{(s)}(\nu l),$$
$$S_l^+ = (2S_\tau + 1)\beta_\uparrow^{(t)+}(l\tau)\beta_\downarrow^{(t)+}(\tau l) = -(2S_l + 1)\alpha_\downarrow^{(s)}(l\nu)\alpha_\uparrow^{(s)}(\nu l) \quad (13)$$

and

$$\hat{n}_{\tau\sigma} + \hat{n}_\tau/(2S_\tau) = (2S_\tau + 1)\beta_\sigma^{(t)}(\tau l)\beta_\sigma^{(t)+}(\tau l),$$
$$\hat{S}_\tau^+ = (2S_\tau + 1)\beta_\downarrow^{(t)}(\tau l)\beta_\uparrow^{(t)+}(\nu l),$$
$$\hat{n}_{\nu\sigma} = (2S_l + 1)\alpha_{\bar{\sigma}}^{(s)+}(\nu l)\alpha_{\bar{\sigma}}^{(s)}(l\nu),$$
$$\hat{S}_\nu^+ = -(2S_l + 1)\alpha_\uparrow^{(s)+}(\nu l)\alpha_\downarrow^{(s)}(l\nu), \quad (14)$$

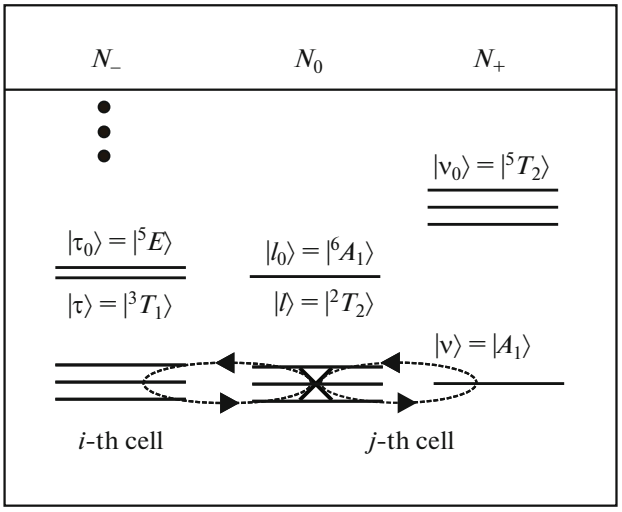

Fig. 3. Spin crossovers $S_{l_0} = 5/2 \leftrightarrow 1/2$, $S_{\tau_0} = 2 \leftrightarrow 1$, and $S_{\nu_0} = 2 \leftrightarrow 0$ in sectors N_0 and N_-, respectively, as well as the superexchange FM interaction for FBO_3 under a high pressure $P > P_{C_2}$.

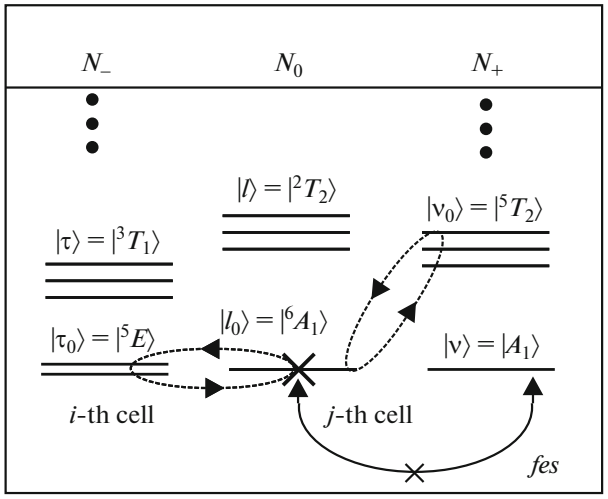

Fig. 4. Spin crossover $S_{\nu_0} = 2 \leftrightarrow 0$ in sector N_+ and the superexchange AFM interaction for $FeBO_3$ under pressure $P_{C_2} > P > P_{C_1}$. Semi-ellipse indicates the forbidden *fes* states that are absent in the superexchange.

where

$$\hat{n}_\tau = \sum_\sigma \hat{n}_{\tau\sigma}.$$

Using these relations in the calculation of the commutator in expression (9), we collect the spin variables into separate terms and sum over all (i, j) pairs. Depending on the combination of indices k and k', two different contributions to spin Hamiltonian $\hat{H}_s = H_s^{AFM} + H_s^{FM}$ in relation (9) are possible. If states $|\nu\rangle$ and $|\tau\rangle$ belong to identical spin partners (e.g., $|^5T_2\rangle$ and $|^5E\rangle$ in Fig. 2), which corresponds to the combination of s and t in relations (11) and the primed symbol of summation over l, ν, and τ, we have

$$\hat{H}_s^{AFM} = \sum_{i\neq j}\sum_{l\tau\nu}{}' \left\{ \frac{J_{ij}(l\tau, l\nu)}{(2S_\tau + 1)(2S_l + 1)} \left(\hat{S}_{il}\hat{S}_{jl} - \frac{1}{4}\hat{n}_{il}\hat{n}_{jl} \right) - \frac{J_{ij}(l\tau, l\nu)}{(2S_\tau + 1)(2S_l + 1)} \left(\hat{S}_{i\tau}\hat{S}_{j\nu} - \frac{1}{2}\hat{n}_{i\tau}\hat{n}_{j\nu} \right) \right\}, \quad (15)$$

where exchange interaction constant is $J_{ij}(l\tau, l\nu)/(2S_\tau + 1)(2S_l + 1)$ and $J_{ij}(l\tau, l\nu) = 2(t_{ij}^{l\tau,l\nu})/\Delta_{l\tau\nu}$. The first term in expression (15) corresponds to the conventional AFM superexchange with correction by factor $(2S_\tau + 1)^{-1}(2S_l + 1)^{-1}$, which is associated with its one-electron nature, and is additive in virtual states $|\nu(\tau)\rangle$ in sectors $N_\pm$.

The contribution from the second term in expression (15) corresponds to the superexchange interaction between a hole in the valence band and an electron in the conduction band. At low temperatures, the contribution to the magnetic energy of the material from this interaction is close to zero, since there are no carriers in the conduction band and the valence band. The superexchange in the Hubbard model does not contain this contribution since these states can only be spin singlets. This contribution can differ from zero in doped materials or in materials under optical pumping [7]. However, the form of this contribution is not determined in this case because, in contrast to the first term in expression (15), it is additive in excited states $|l\rangle$ of the magnetic ion. The contributions with different signs are summed over l because $\Delta_{l\tau\nu}$ can assume both positive and negative value for excited states $|l\rangle$.

On the other hand, if $|\nu\rangle$ and $|\tau\rangle$ belong to different spin partners (e.g., states $|^3T_1\rangle$ and $|A_1\rangle$ in Fig. 3), which corresponds to the combination of s and s or t and t in expression (11) and to the double-primed summation symbol, the superexchange interaction reverses its sign:

$$\hat{H}_s^{FM} = -\sum_{i\neq j}\sum_{l\tau\nu}{}'' \frac{J_{ij}(l\tau, l\nu)}{(2S_\tau + 1)(2S_l + 1)} \left(\hat{S}_{il}\hat{S}_{jl} + \frac{3}{4}\hat{n}_{il}\hat{n}_{jl} \right), \quad (16)$$

where the sum contains no terms at all and $\hat{H}_s^{FM} = 0$ (i.e., there exists the AFM ordering) because of the maximal spin $S_{l_0} = 5/2$ at the Fe^{3+} ion in undeformed $FeBO_3$. There is no contribution in expression (16) from the exchange interaction between a hole and an electron because $\hat{H}_s^{FM} \neq 0$ for deformed $FeBO_3$ with a set of spins $S_{l_0} = 1/2$, $S_{\nu_0} = 0$, and $S_{\tau_0} = 1$ in Fig. 3, but the spin of the *fes* quasiparticle in the conduction band is equal to S_{ν_0} (i.e., to zero).

Expressions (15) and (16) do not contain non-Heisenberg contributions with allowance for the orbital degrees of freedom [10, 28], which appear in

Table 1

δ	Electron configuration	Magnetic ordering
δ_+	d^6, $S_{\nu_0} = 0$, N_+	FM, T_C
	d^4, $S_{\tau_0} = 1$, N_-	
	$d^5(Fe^{3+}, Mn^{2+})$, $S_{l_0} = \frac{1}{2}$, N_0	
δ_-	$d^5(Fe^{3+}, Mn^{2+})$, $S_{l_0} = \frac{5}{2}$, N_0	AFM, T_N
	d^4, $S_{\tau_0} = 2$, N_-	
	d^6, $S_{\nu_0} = 2$, N_+	

fact in initial Hamiltonian (9). Such contributions were calculated in [7] for a magnetic semiconductor under optical pumping at the frequency of the d–d transitions (exciton excitations), where multielectron states form the complete set

$$\sum_l |l\rangle\langle l| = 1$$

of eigenvectors in the one-cell model, and operators

$$\hat{\tau}^{(\pm)} = X_i^{ll'}, \quad \hat{\tau}^z = \frac{1}{2}(X_i^{ll} - X_i^{l'l'}),$$

which form the pseudospin commutation relations, determine the probability of a transition from state $|l\rangle$ to state $|l'\rangle$ under optical pumping. Analysis of such exciton excitations in the superexchange is beyond the scope of this paper; here, we are interested in certain conclusions concerning the exchange interaction between ions in states with an arbitrary multiplicity (including different spin multiplicities).

In view of different combinations of indices t and s in expression (11), in the derivation of the expression for the exchange interaction constant in relations (15) and (16), the sign of this constant is independent of spin S_l at the magnetic ion, but is completely determined by the spin origin of the virtual states (these can be high-spin or low-spin partners $|\tau\rangle$ and $|\nu\rangle$ relative to the ground state of the magnetic ion with $\delta(S_{\nu_0(\tau_0)}, S_l \pm |\sigma|) \neq 0$). The exchange constant in the first term in expressions (15) and (16) is additive in quasiparticles with participation of states $|\tau\rangle$ and $|\nu\rangle$. The main contribution comes from *frs* and *fes* quasiparticles in Fig. 1 because the denominator $\Delta_{l\tau\nu}$ in the exchange constant is the smallest for them. However, these quasiparticles can be absent in the material in view of the equality of the matrix elements in expression (4) to zero [24]. Orienting our analysis onto to the main contribution, we arrive at the conclusion that the superexchange is antiferromagnetic if two identical high-spin or low-spin partners with $S_{\nu_0} = S_{\tau_0}$ are involved in it. If, however, virtual partners $|\tau_0\rangle$ and $|\nu_0\rangle$ belong to different categories, the FM ordering occurs.

3. SUPEREXCHANGE INTERACTION IN IRON BORATE UNDER PRESSURE. CONCLUSIONS

1. The type (AFM or FM) of the superexchange interaction is determined by the combination of high-spin and low-spin virtual $|\tau_0\rangle$ and $|\nu_0\rangle$ partners in the $N_\pm$ sectors of the configuration space (see Fig. 1) for ground state $|l_0\rangle$ of the magnetic ion with the selection rule $\delta(S_{\nu_0(\tau_0)}, S_{l_0} \pm |\sigma|) \neq 0$. If two identical high-spin or low-spin partners with the condition $S_{\nu_0} = S_{\tau_0}$ are involved in the main contribution, the superexchange is of the AFM type. If, however, partners $|\tau_0\rangle$ and $|\nu_0\rangle$ belong to different spin categories with $S_{\nu_0} = (S_{\tau_0} \pm 1)$, we have the FM ordering. For example, in the Hubbard model with $S_{l_0} = 1/2$ and one state $|l\rangle$ per cell ($S_{\nu_0} = S_{\tau_0} = 0$), we have the AFM ordering. Analogously to La214 cuprates with low-spin terms, for which the situation in the Hubbard model is realized, the AFM ordering is also observed for ground state of iron borate ($S_{\nu_0} = S_{\tau_0} = 2$; see Fig. 2). Analogous conclusions were also drawn in [9, 10] for the superexchange between localized spins in the Hubbard model with degeneracy.

It is interesting to note that a simple consequence of this statement is the absence of a dependence of the magnetic ordering type on the spin crossover for the ground state $|l_0\rangle$ of the magnetic ion. However, the crossover can eliminate the main contributions from *frs* and (or) *fes* quasiparticles to the superexchange interaction, due to a change in the matrix elements of electron excitations; in this case, its type is determined by the spin origin of the first excited states $|\tau\rangle$ and $|\nu\rangle$. The superexchange interaction can also be changed under optical pumping of only one of the ions in a magnetically coupled pair [7] or under the concomitant spin crossover for the ground states in the $N_\pm$ sectors. In fact, we have a complete spin crossover accompanying changes in the crystal field δ. Using such a helpful microscopic interpretation of the Goodenough–Kanamori rules for the 180°-superexchange [29, 30], we represent our conclusions concerning the type of magnetic ordering in the form of Table 1. Since the crossover is induced by the competition between crystal field δ = 10 Dq and Hund exchange J_H, we have formulated the qualitative conclusions for the electron configurations in the vicinity of half-filling of the d shell for weak ($\delta_- \ll J_H$) as well as strong ($\delta_+ \gg J_H$) octahedral field relative to the Hund exchange.

The evolution of the magnetic order is determined by a sequence of spin crossovers in sectors $N_\pm$ and N_0 upon an increase in pressure. If $\delta(M_{\tau(\nu)_0}, M_{l_0} + \sigma) = 0$ and symmetry prohibits the *frs* and (or) *fes* quasiparticles (see Fig. 4), the dependence of the superexchange on S_{l_0} as a result of spin crossover is observed only in sector N_0. In the case of full crossover $\delta_- \rightleftarrows \delta_+$, the

rule relating the ordering type with spins S_{ν_0} and S_{τ_0} holds well.

2. Let us consider in greater detail the conclusions directly related to the P/T phase diagram for $FeBO_3$ [2]. For this purpose, we can use the system of simple estimates [31, 32], where the energy of terms in sector N_0 can be written in the form

$$\begin{aligned} E_{hs} &= E_c(d^5) - 10J_{\mathrm{H}}, \\ E_{is} &= E_c(d^5) - 10Dq - 6J_{\mathrm{H}}, \\ E_{ls} &= E_c(d^5) - 20Dq - 4J_{\mathrm{H}}, \end{aligned} \tag{17}$$

for spins $S_l = 5/2$, $3/2$, and $1/2$, respectively. It follows hence that spin crossover $S_l = 5/2 \leftrightarrow 1/2$ in the ground state is possible for $\delta = 3J_{\mathrm{H}}$ in accordance with a certain pressure P_{C_2}. Here and below, $E_c(d^n)$ is the part of the energy of the term [32], which is independent of exchange J_{H} and crystal field $\delta(P)$.

Analogously, in sector N_+, for the d^6 configuration, we have

$$\begin{aligned} E_{hs} &= E_c(d^6) - 4Dq - 10J_{\mathrm{H}}, \\ E_{is} &= E_c(d^6) - 14Dq - 7J_{\mathrm{H}}, \\ E_{ls} &= E_c(d^6) - 24Dq - 6J_{\mathrm{H}}, \end{aligned} \tag{18}$$

for spins $S_{\nu_0} = 2$, 1, and 0, respectively. It can be seen that spin crossover $S_{\nu_0} = 2 \leftrightarrow 0$ in the ground state is possible for $\delta = 2J_{\mathrm{H}}$ in accordance with a certain pressure $P_{C_1} < P_{C_2}$. Analogously, in sector N_-, for the d^4 configuration, we have

$$\begin{aligned} E_{hs} &= E_c(d^4) - 6Dq - 6J_{\mathrm{H}}, \\ E_{is} &= E_c(d^4) - 16Dq - 3J_{\mathrm{H}}, \\ E_{ls} &= E_c(d^4) - 16Dq - 2J_{\mathrm{H}}, \end{aligned} \tag{19}$$

for spins $S_{\tau_0} = 2$, 1, and 0, respectively. It follows hence that spin crossover $S_{\tau_0} = 2 \leftrightarrow 1$ in the ground state is possible for the same values of crystal field $\delta = 3J_{\mathrm{H}}$ as for d^5. Applying the results compiled in Table 1 to these calculations, we can establish the sequence in the variation of the superexchange interaction with increasing pressure (see Fig. 5):

(i) $P < P_{C_1}$, $\delta < 2J_{\mathrm{H}}$, and all ground states on the level diagram in Fig. 2 are high-spin states. Consequently, *frs* and *fes* quasiparticles contribute only to $\hat{H}_s^{\mathrm{AFM}}$, and the inequality $\hat{H}_s^{\mathrm{AFM}} \gg \hat{H}_s^{\mathrm{FM}}$ holds (AMF order).

(ii) A spin crossover of virtual states d^6 and $2J_{\mathrm{H}} < \delta < 3J_{\mathrm{H}}$ has occurred. The spin at the magnetic ion has not changed, and previous AFM ordering exists due to the prohibition of the existence of *fes* quasiparticles in the pressure range $P_{C_1} < P < P_{C_2}$ with the energy level diagram shown in Fig. 4.

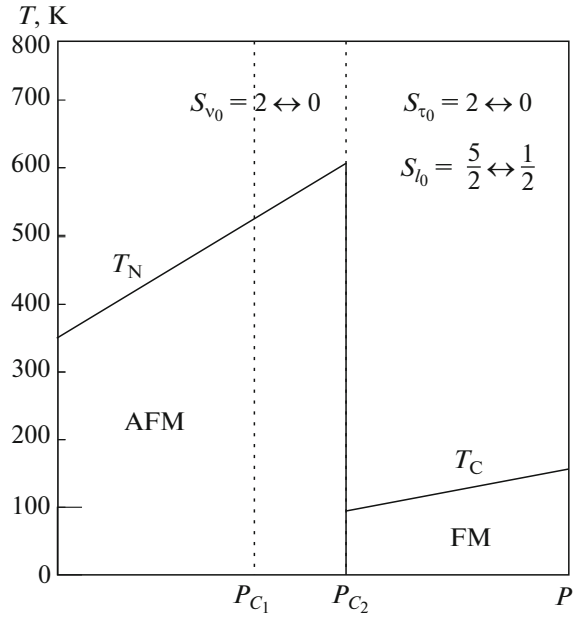

Fig. 5. Spin crossovers and magnetic phase P/T diagram for $FeBO_3$.

(iii) $P > P_{C_2}$ and $\delta > 3J_{\mathrm{H}}$; the spin crossover for both occupied and virtual states with energy level diagram from Fig. 3 has occurred. In accordance with the rule for the main contribution, the FM ordering takes place. In this case, *frs* and *fes* quasiparticles contribute only to $\hat{H}_s^{\mathrm{FM}}$; i.e., $\hat{H}_s^{\mathrm{FM}} \gg \hat{H}_s^{\mathrm{AFM}}$.

We can also estimate the ratio of critical temperatures for the applied pressure close to critical value P_{C_2} in Fig. 5. Indeed, it follows from the mean-field estimate of the form $T_{\mathrm{N}} \sim JzS(S+1)/3$ [33, 34], where the exchange constant is taken from expression (15), that this relation has the form

$$\begin{aligned} &\frac{T_{\mathrm{C}}(P \geq P_{C_2})}{T_{\mathrm{N}}(P \leq P_{C_2})} \\ &= \left[\frac{(5/2)\cdot(7/2)}{30}\right] \Big/ \left[\frac{(1/2)\cdot(3/2)}{6}\right] \approx 0.2. \end{aligned} \tag{20}$$

Therefore, for ions in the d^5 configuration in an octahedral field, the type of magnetic ordering changes upon an increase in pressure from the AFM to FM ordering.

It should also be noted that the phase diagram in Fig. 5 differs from the diagram constructed using a phenomenological approach [2], in which the superexchange constant is independent of spin at the magnetic ion. In contrast to this diagram, we have the FM ordering at high pressures with critical temperature $T_{\mathrm{C}} \approx 0.2T_{\mathrm{N}}$.

The existence of magnetic ordering at $P > P_{C_2}$ ($P_{C_2} \approx 50$ GPa) on the experimental phase diagram

constructed from the Mössbauer measurements is confirmed [2], and the relation between the critical temperatures is in conformity with estimate (20). However, the type of magnetic ordering at high pressures remains unclear as yet.

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