PHYSICAL REVIEW B **84**, 014415 (2011)

Superexchange mechanisms in an ideal $3d^1$ cubic system of the perovskite type

J. Choukroun
School of Physics and Astronomy, Raymond and Beverly Sackler Faculty of Exact Science, Tel Aviv University, Tel Aviv 69978, Israel

(Received 10 September 2008; revised manuscript received 13 December 2010; published 25 July 2011)

In this article we extend the expression obtained by Kugel and Khomskii for cubic perovskites, where the transition metal ion has a $3d^1$ electronic configuration with threefold ($3dt_{2g}$) orbital degeneracy. We derive an effective spin-orbital Hamiltonian by taking into account both the role of the oxygen on the bond between the transition metal ions and the role of the $3de_g$ levels in superexchange processes, while no simplifications are done concerning the electron-electron interactions. A simple mean-field treatment yields a competition between an antiferromagnetic (AFM) and a ferromagnetic phase. The stability of these phases is driven by several parameters including the following: the ratio $t_\pi/t_\sigma = |(pd\pi)/(pd\sigma)|$ between π-type and σ-type electron hoppings, the charge transfer gap Δ_{CT}, the exchange (Hund's) coupling, the crystal field Δ_0 between the t_{2g} and e_g $3d$ orbitals, and the "pseudo" crystal field gap Δ_{zx}^{oxy} between the oxygen $2p$ orbitals. The addition of the spin-orbit coupling is shown to be able to lead to a sensible reduction of the ordered magnetic moment in the AFM phase as well as the appearance of a weak ferromagnetic moment.

DOI: 10.1103/PhysRevB.84.014415 PACS number(s): 75.30.Et, 75.10.Dg, 71.10.−w

I. INTRODUCTION

As is well known, the magnetic interaction in magnetic insulators with partially filled *d* shells is due to superexchange processes occurring between two metallic magnetic ions (M) via an intermediate ligand [generally the oxygen (O)]. For orbitally nondegenerate systems the magnitude and the sign of this interaction depend on the geometry of the metal-oxygen-metal (M-O-M) bond and can generally be predicted using the so-called Goodenough-Kanamori-Anderson rules.[1] According to these rules, the leading isotropic superexchange for a M-O-M bond of 180° is strongly antiferromagnetic (AFM) while it is ferromagnetic (FM) and much weaker in a 90° M-O-M bond. For orbitally degenerate systems the situation is much more complex: first because both spin and orbital degrees of freedom are involved, secondly because the number of electrons (or holes) occupying the relevant orbitals plays an important role, and thirdly because the presence of (Jahn-Teller) distortions can utterly change the physics. In particular, the perovskite-type oxide family RMO_3 where R denotes a trivalent rare-earth ion ($R = La,Y,\ldots$) and $M = Ti,V,\ldots$ allows the study of the rich magnetic and electronic properties caused by this interplay of parameters. Such systems are generally described by Kugel and Khomskii (KK)-type Hamiltonians.[2–5] In these theoretical models, the M-O-M bond is replaced by an effective M-M bond and distortions are often neglected. This generally leads to a satisfactory description of the experimental results, except for the apparently most simple $3d^1$ systems $RTiO_3$ ($R = La, Y$).[4,6–8] In these Mott-Hubbard insulators, each Ti^{3+} ion is located at the center of an oxygen octahedron.[9] As is well known, such a surrounding lifts partially the $3d$ orbital degeneracy into t_{2g} symmetry (of lower energy) for (d_{xy},d_{yz},d_{xz}) orbitals, and e_g symmetry (of upper energy) for $d_{x^2-y^2}$ and d_{z^2} orbitals. In this case, a KK-type Hamiltonian essentially predicts a FM ground state, observed in $YTiO_3$ but not in $LaTiO_3$ which is a G-type antiferromagnet.[4,10] Still there is no commonly accepted view on the origin of superexchange peculiarities in these systems and two different theories have been proposed to explain these observations: The first one emphasizes the relative weakness of the Yahn-Teller coupling in $LaTiO_3$ (as compared to the much more distorted compound $YTiO_3$); for such a system for which the degeneracy of t_{2g} orbital state is present, it is necessary to take into account the dynamic effects in which the orbitals may form a coherent orbital-liquid state stabilized by quantum effects.[4,6,7,11–13] In this frame, several experimental results can be successfully explained and, in particular, the spin reduction[6,7,10] observed in $LaTiO_3$. On the contrary, the second approach emphasizes the existence of lattice distortions even in $LaTiO_3$, removing the t_{2g} orbital degeneracy and stabilizing the orbital structure. In such a case the phase stability criteria can change leading to the isotropic superexchange sign shift when one moves through the rare-earth series from $YTiO_3$ (FM) to $LaTiO_3$ (AFM). This question is widely discussed in the literature.[5,10,14–23] Therefore it is especially clear from the papers by Khaliullin *et al.*, Mochizuki and Imada, Schmitz *et al.*, and Solovyev (which deal with different methods of orbital state and superexchange interactions calculations) that in various approaches one can find mechanisms of stabilization ferromagnetism in $YTiO_3$ and antiferromagnetism in $LaTiO_3$. Nevertheless, all these works are assuming that the M-O-M bond can be replaced by an effective M-M bond. In the present work we propose to improve the KK model by considering in more detail the role of the oxygen in superexchange processes and to know whether one can obtain more easily the AFM state in the cubic symmetric case (still without distortions). Here we show that this is indeed possible.

Starting from a microscopic Hamiltonian describing hopping processes between titaniums and oxygens and assuming cubic symmetry, we propose here to consider the importance of the combined presence of the oxygen and of the e_g levels in superexchange processes and their possible consequences on the magnetic properties of $3d^1$ compounds. Indeed as shown in Fig. 1(a), if we consider a bond $i - j$ in the $\mathbf{z}$ direction two kinds of electron hoppings can happen: a σ-type electron hopping between oxygen orbital $2p_z$ and titanium orbital d_{z^2}, and a π-type electron hopping between oxygen orbitals ($2p_x$,$2p_y$) and titanium orbitals (d_{xz},d_{yz}). As shown

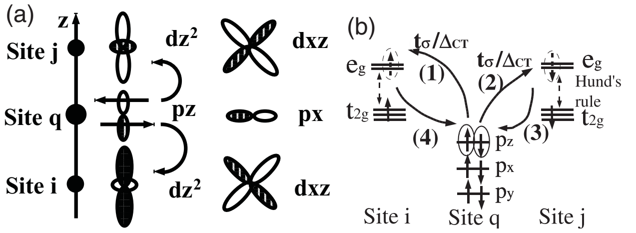

FIG. 1. (a) σ-type hoppings between oxygen orbital $2p_z$ and titanium orbital d_{z^2} (left-hand side) and π-type hoppings between oxygen orbitals $[2p_x(2p_y)]$ and titanium orbitals $[d_{xz}(d_{yz})]$ (right-hand side). (b) Effective spin-spin interaction between site i and site j assuming σ-type hoppings only between the oxygen and the titaniums. Due to Hund's rule, the resulting effective interaction is AFM.

in Fig. 1(b), if we neglect π-type electron hoppings and keep only σ-type electron hoppings $[(pd\pi) = 0$ and $(pd\sigma) \neq 0$ in terms of the Slater and Koster parameters],[24] only the $2p_z$ electrons can delocalize: In the first step [denoted by (1) in Fig. 1(b)] one of the $2p_z$ electrons is virtually transferred onto the titanium d_{z^2} (e_g) orbital on site i. Due to Hund's rule, the initial t_{2g} electron and the transferred one have the same spin orientation. The same phenomenon occurs in step (2): The remaining $2p_z$ electron of opposite spin is virtually transferred onto titanium site j. Due to Hund's rule, the resulting spin-spin interaction between the t_{2g} electrons occupying site i and j is AFM. In steps (3) and (4), the virtually transferred electrons return to the oxygen. Due to the particular crystallography of these materials [see Fig. 2(a)], no frustration will appear leading to a G-type antiferromagnet.

On the other hand, if we consider only π-type electron hoppings $[(pd\pi) \neq 0$ and $(pd\sigma) = 0]$ we will generally finish with a FM interaction,[2,4] as illustrated in Fig. 3. In Fig. 3(a), a $2p_x$ (or $2p_y$) electron of spin σ is virtually transferred to site i, preferentially on one of the unoccupied orbitals due to Coulombic repulsion. In step (2) the oxygen hole is filled by the electron coming from site j with the same spin σ. These two steps are therefore equivalent to an effective electron hopping between the titaniums, as usually used in KK-type models, in contrast with the σ-type hopping presented above. Due to Hund's rule, the resulting spin-spin interaction between site i and j is FM. For similar reasons, the case with two holes on the oxygen shown in Fig. 3(b) will also lead preferentially to an FM interaction.

A competition will therefore occur between these two pictures. The following parameters are then of crucial importance:

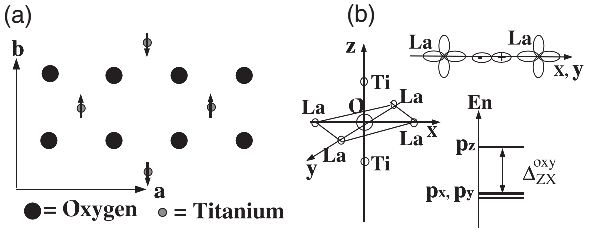

FIG. 2. (a) Crystal structure in the (a,b) plane. (b) Oxygen local environment and suggestive orbital couplings between the $(2p_x,2p_y)$ oxygen orbitals and the La ions in $LaTiO_3$.

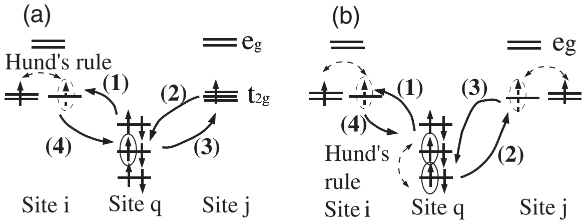

FIG. 3. π-type hoppings between oxygen orbitals and titanium orbitals favoring an effective ferromagnetic coupling. While the scenario represented in (a) can be mapped onto an effective M-M transfer, the second one [represented in (b)] with two holes on the oxygen intermediate state cannot be.

(i) the ratio $t_\pi/t_\sigma = |(pd\pi)/(pd\sigma)|$; as we have seen, the smaller it is, the larger the antiferromagnetic interaction will be. In fact, it is clear that this quantity is small, as σ-type hoppings between the ions are creating the chemical bond responsible for the stability of the crystal. The $2p_z$ electrons of Fig. 1 are then "naturally" delocalized on the neighboring titaniums. (ii) The charge transfer energy $\Delta_{\mathrm{CT}}(n,U) = \epsilon_d - \epsilon_n + U - 5(V - 2K)$ involving the energy gap $\epsilon_d - \epsilon_n$ between the $3d$ t_{2g} and the $2p_n$ orbitals, the Coulombic energy U (V) on the titanium (oxygen), and Hund's coupling K on the oxygen. This quantity corresponds to the cost in energy to transfer one electron from a fully occupied oxygen to the T_i^{3+} ion. As the order of magnitude of the σ-type hopping process is $(-t_\sigma) \times (t_\sigma/\Delta_{CT})^3$ (see Fig. 1 and below) while the order of magnitude of the main competing π-type process [represented in Fig. 3(a)] corresponding to the usual description of $RTiO_3$ in terms of effective transfer integrals between the titaniums is $-t_{\mathrm{eff}}^2/U$, with $t_{\mathrm{eff}} = t_\pi^2/\Delta_{\mathrm{CT}}$, small $\epsilon_d - \epsilon_n$ values and large $V - 2K$ and U values (when $U < \epsilon_d - \epsilon_n$) are thus expected to favor the AFM process. (iii) Hund's coupling I (K) on the titanium (oxygen), π-type process being of order I and σ-type process of order I^2. (iv) The value of the gap between the t_{2g} and e_g levels. In real perovskite systems, the measured value is around $\Delta_{dd} \simeq 1.7 - 2.8$ eV[5,19,25] which is not favorable to σ-type hopping processes. However, it is well known in inorganic chemistry that this gap is the sum of the crystal field gap Δ_0 and the ligand field gap Δ_{LF} $(\Delta_{dd} = \Delta_0 + \Delta_{\mathrm{LF}})$. Generally Δ_0 is expected to be very small $\Delta_0 \sim 0 - 0.5$ eV and is often neglected in computational treatments and in band structure calculations,[26] while Δ_{LF} comes from electron hoppings between the titanium and the other ions (mainly the first neighbor oxygens). Therefore, in perturbative expansion in the hopping term (as we propose to perform) only Δ_0 has to be considered. (v) The gap $\Delta_{zx}^{oxy} = \epsilon_{p_z} - \epsilon_{p_x}$ between the oxygen orbital $2p_z$ and the degenerate oxygen orbitals $2p_x$ and $2p_y$ [Fig. 2(b)]. As already discussed for the titanium, this gap is the result of the crystal field and of the ligand field and only the first one (which is small) should have to be considered $(\Delta_{zx}^{oxy} \simeq 0.21$ eV as reported in[27] for $SrTiO_3$). But another problem emerges for the oxygen as its surrounding is also composed of R^{3+} ions. Therefore, in a microscopic Hamiltonian describing hoppings between titaniums and oxygens only, the oxygen orbitals must be considered as already coupled with the R^{3+} ions and still not with the Ti^{3+} ions, this last hybridization being precisely described by the microscopic Hamiltonian. As shown in Fig. 2(b), this leads to an important contribution of the ligand field energy for orbitals $2p_x$ and $2p_y$ ($2p_x$ and $2p_y$ electrons being "naturally" delocalized on the R^{3+} ions, therefore creating the chemical σ bonds with the R^{3+} ions), orbital $2p_z$ remaining (quasi) unchanged. The resulting gap Δ_{zx}^{oxy} that we have to consider in the microscopic Hamiltonian is then much more important than the gap from crystal field alone, and is also very different from the one obtained in band structure calculations (containing all the hybridizations). The ionization of $2p_z$ electrons is then much easier than the ionization of those occupying $2p_x$ and $2p_y$ orbitals, thus favoring σ-type electron hoppings. From the last three points, a more precise estimate for the σ- and π-type main competing processes is obtained using $\Delta_{\rm CT}^{(\sigma)} = \Delta_{\rm CT}(2p_x, U - I + \Delta_0 - \Delta_{zx}^{oxy})$ and $\Delta_{\rm CT}^{(\pi)} = \Delta_{\rm CT}(2p_x, U - I)$, respectively.

The inclusion of such a σ-type process leads then to an AFM process, and one can note that this process is also expected to occur in $3d^2$ and $3d^3$ compounds (in which the electrons are only in the t_{2g} states). As the usual KK Hamiltonian already predicts AFM in these two cases (in agreement with the experiments) and essentially FM in $3d^1$ compounds, the inclusion of such a σ-type electron hopping has really a decisive incidence only in this last case. In this frame, the difference between $LaTiO_3$ and $YTiO_3$ could be a good demonstration of the existence and of the important role played by this AFM process, in competition with the FM π-type electron one.

Following all the preceding remarks, our microscopic Hamiltonian $\mathcal{H}$ will be represented by the sum of two terms: a main Hamiltonian $\mathcal{H}_0$ describing free electrons and Coulombic interactions, and a perturbative one $\mathcal{V}$ describing hopping processes between oxygens and titaniums; $\mathcal{H} = \mathcal{H}_0 + \mathcal{V}$ with

$$\begin{aligned}\mathcal{H}_0 = {} & \sum_{i\alpha\sigma} \epsilon_\alpha d^+_{i\alpha\sigma} d_{i\alpha\sigma} + \frac{1}{2} \sum_{i,\alpha,\beta,\gamma,\delta,\sigma,\sigma'} U_{\alpha\beta\gamma\delta} d^+_{i\alpha\sigma} d^+_{i\beta\sigma'} d_{i\gamma\sigma'} d_{i\delta\sigma} \\ & + \sum_{qn\sigma} \epsilon_n p^+_{qn\sigma} p_{qn\sigma} + \frac{1}{2} \\ & \times \sum_{q,n_1n_2n_3n_4,\sigma,\sigma'} V_{n_1n_2n_3n_4} p^+_{qn_1\sigma} p^+_{qn_2\sigma'} p_{qn_3\sigma'} p_{qn_4\sigma},\end{aligned} \tag{I.1}$$

$$\mathcal{V} = \sum_{iq\alpha n\sigma} \left(t^{\alpha n}_{iq} d^+_{i\alpha\sigma} p_{qn\sigma} + t^{n\alpha}_{qi}\, p^+_{qn\sigma} d_{i\alpha\sigma} \right). \tag{I.2}$$

Here, $d^+_{i\alpha\sigma}$ ($p^+_{qn\sigma}$) creates an electron on titanium (oxygen) site i (q), $3d$ orbital α ($2p$ orbital n), spin σ, energy ϵ_α (ϵ_n); $t^{\alpha n}_{iq}$ is the hopping matrix element between titanium i orbital α, and oxygen q orbital n while $U_{\alpha\beta\gamma\delta}$ and $V_{n_1n_2n_3n_4}$ are the Coulombic terms on titanium and oxygen ions. The axis for the $3d$ orbitals referring to the oxygen octahedra, ϵ_α, will be $\epsilon_\alpha = \epsilon_0$ for $\alpha \in t_{2g}$ and $\epsilon_\alpha = \epsilon_0 + \Delta_0$ for $\alpha \in e_g$. In the particular case of a cubic symmetry, the transfer integral $t^{\alpha n}_{iq}$ will be given by

$$t^{\alpha n}_{iq} = \delta_{nn_\alpha} \left(t^\pi_{iq} (\delta_{\alpha,xz} + \delta_{\alpha,yz}) + t^\sigma_{iq} \delta_{\alpha,z^2} \right), \tag{I.3}$$

which precisely define $t_\pi = |t^\pi_{iq}|$ and $t_\sigma = |t^\sigma_{iq}|$. In (I.3), the axes are referring to Fig. 1 while n_α corresponds to oxygen orbital $2p_x$ for titanium orbital $\alpha = d_{xz}$, $2p_y$ for $\alpha = d_{yz}$, and $2p_z$ for $\alpha = d_{z^2}$. For the Coulombic terms, $U_{\alpha\beta\gamma\delta}$ is expressed in terms of the Racah parameters $\mathcal{A}$,$\mathcal{B}$,$\mathcal{C}$[28] while $V_{n_1n_2n_3n_4}$ reads

$$V_{n_1n_2n_3n_4} = (1 - \delta_{n_1n_2}) \{ \delta_{n_1n_4} \delta_{n_2n_3} V' + \delta_{n_1n_3} \delta_{n_2n_4} K \} + \delta_{n_1n_2n_3n_4} V, \tag{I.4}$$

with $V' = V - 2K$. For the numerical values we will take $\epsilon_d - \epsilon_n = 5.91$ eV,[29] $t_\sigma = 2.4$ eV,[30] $U = 3.5$ eV, $\mathcal{B} = 0.1$ eV[19,26] (i.e., $\mathcal{A} = 1.9$ eV, $I = 0.7$ eV) reported for $RTiO_3$ systems and typical values for the following parameters: $\Delta_0 \simeq 0.5$ eV, $\Delta_{zx}^{oxy} \simeq 1$ eV, $V \simeq 1.76$ eV, $K \simeq 0.6$ eV [$V - 2K \simeq 0.56$ eV being obtained by taking $\Delta_{\rm CT}(2p_x, U' - I) \simeq 4.5$ eV[31] with $U' = U - 2I$] and $\lambda \simeq 0.02$ eV.[32] In terms of the Racah parameters we will have $U = \mathcal{A} + 4\mathcal{B} + 3\mathcal{C}, I = 3\mathcal{B} + \mathcal{C}$ which means $\mathcal{A} = 1.9$ eV, $\mathcal{B} = 0.1$ eV when taking $\mathcal{C} \simeq 4\mathcal{B}$.[28]

This article will be organized as follows: In part II we will derive the effective spin-orbital Hamiltonian in a very general way. In particular we will see how the spin part (isotropic spin-spin interaction) of the Hamiltonian can always be computed independently of the orbital part even for systems with more than one electron occupying the $3d$ orbitals. Part III presents the mean-field phase diagram obtained using this model, predicting G-AFM, C-AFM, and FM phases. The emergence and the stability of the AFM phases is discussed. In particular, we show that they are favored by small values of $t_\pi / t_\sigma, \Delta_0$ and high values of Δ_{zx}^{oxy}, $\mathcal{A}$, $\mathcal{B}$, and $V - 2K$. Finally, the addition of the spin-orbit coupling is presented in part IV and is shown to allow a sensible reduction of the magnetic moment and to lead to the appearance of a weak ferromagnetic moment as observed in $LaTiO_3$.

II. DERIVATION OF THE EFFECTIVE HAMILTONIAN

In this part, we will derive an effective spin-orbital Hamiltonian for the t_{2g} orbitals, involving the e_g levels during hopping processes. Due to the presence of the oxygen between each pair of titanium ions, an expansion up to order four in $\mathcal{V}$ is necessary to obtain a spin-orbital Hamiltonian. $\mathcal{P}$ denoting the projector on the states with one electron per each titanium site and fully occupied oxygen $2p$ orbitals, and $\mathcal{P}_{t_{2g}}$ denoting the projector on the degenerate ground state (of energy E_0) of the unperturbed Hamiltonian $\mathcal{H}_0$ with one electron per each titanium site occupying a t_{2g} orbital, the spin-orbital Hamiltonian $\tilde{\mathcal{H}}_4$ is given by[33–35]

$$\tilde{\mathcal{H}}_4 = \tilde{\mathcal{H}}_{4,1} + \tilde{\mathcal{H}}_{4,2}, \tag{II.1}$$

with

$$\tilde{\mathcal{H}}_{4,1} = \mathcal{P}_{t_{2g}} \mathcal{V} \frac{-\mathcal{Q}}{\mathcal{H}_0 - E_0} \mathcal{V} \frac{-\mathcal{Q}}{\mathcal{H}_0 - E_0} \mathcal{V} \frac{-\mathcal{Q}}{\mathcal{H}_0 - E_0} \mathcal{V} \mathcal{P}_{t_{2g}}, \tag{II.2}$$

$$\begin{aligned}\tilde{\mathcal{H}}_{4,2} = -\frac{1}{8} \sum_k \Bigg\{ & \mathcal{P}_{t_{2g}} \mathcal{V} \frac{-\mathcal{Q}}{\mathcal{H}_0 - E_0} \frac{-\mathcal{Q}}{\mathcal{H}_0 - E_k} \mathcal{V} \mathcal{P}_k \mathcal{V} \\ & \times \left(\frac{-\mathcal{Q}}{\mathcal{H}_0 - E_k} + 3 \frac{-\mathcal{Q}}{\mathcal{H}_0 - E_0} \right) \mathcal{V} \mathcal{P}_{t_{2g}} + \text{h.c.} \Bigg\}.\end{aligned} \tag{II.3}$$

In these expressions, $\mathcal{Q} = 1 - \mathcal{P}$ and $\mathcal{Q}/(\mathcal{H}_0 - E_0) = \mathcal{Q}^*(1/\mathcal{H}_0 - E_0)^*\mathcal{Q}$ while $\mathcal{P}_k$ is the projector on a given $\mathcal{H}_0$

eigenstate ψ_k of energy E_k with one electron on each titanium site occupying either a t_{2g} orbital or an e_g one. From the previous expressions, $\tilde{\mathcal{H}}_{4,1}$ will clearly lead to a spin-orbital Hamiltonian while $\tilde{\mathcal{H}}_{4,2}$ will only generate orbital terms. The knowledge of the two-electron $\mathcal{H}_0$ eigenstates is necessary to compute the effective Hamiltonian. As these two electron eigenstates can be characterized by a total spin S ($S = 0$ or $S = 1$), they will be expressed using the two-particle operators:

$$\varphi^{(\sigma)}_{i\alpha\alpha_1}(S=1) = (1-\delta_{\alpha\alpha_1})\left\{\delta_{\sigma\sigma_1}\varphi^{(\sigma)}_{i\alpha\alpha_1}(1{,}2\sigma) + \frac{1}{\sqrt{2}}(1-\delta_{\sigma\sigma_1})\varphi^{(\sigma)}_{i\alpha\alpha_1}(1{,}0)\right\}, \tag{II.4}$$

$$\varphi^{(\sigma)}_{i\alpha\alpha_1}(S=0) = (1-\delta_{\sigma\sigma_1})\left\{\frac{1-\delta_{\alpha\alpha_1}}{\sqrt{2}}\varphi^{(\sigma)}_{i\alpha\alpha_1}(0{,}0) + \delta_{\alpha\alpha_1}\varphi^{(\sigma)}_{i\alpha\alpha_1}(0{,}0)\right\}, \tag{II.5}$$

where α and α_1 denote the two occupied $3d$ orbitals while

$$\varphi^{(\sigma)}_{i\alpha\alpha_1}(1{,}2\sigma) = d^+_{i\alpha\sigma}d^+_{i\alpha_1\sigma}, \tag{II.6}$$

$$\varphi^{(\sigma)}_{i\alpha\alpha_1}(1{,}0) = (1-\delta_{\sigma\sigma_1})\frac{1}{\sqrt{2}}(d^+_{i\alpha\sigma}d^+_{i\alpha_1\sigma_1} + d^+_{i\alpha\sigma_1}d^+_{i\alpha_1\sigma}), \tag{II.7}$$

$$\varphi^{(\sigma)}_{i\alpha\alpha_1}(0{,}0) = (1-\delta_{\sigma\sigma_1})\frac{1}{2^{\frac{1}{2}(1+\delta_{\alpha\alpha_1})}}(d^+_{i\alpha\sigma}d^+_{i\alpha_1\sigma_1} - d^+_{i\alpha\sigma_1}d^+_{i\alpha_1\sigma}). \tag{II.8}$$

Denoting by $|\text{vac}\rangle$ the vacuum state, the use of $\varphi^{(\sigma)}_{i\alpha\alpha_1}(S=1)$ and $\varphi^{(\sigma)}_{i\alpha\alpha_1}(S=0)$ will allow one to express the effective Hamiltonian as a product of an orbital and a spin part. We indeed have $d_{i\alpha_5\sigma_5}d_{i\alpha_3\sigma_3}\varphi^{(\sigma)}_{i\alpha\alpha_1}(S)|\text{vac}\rangle = T^S_{\alpha_1\alpha_5\alpha_3\alpha} \times T_{\sigma_5\sigma_3\sigma_1\sigma}(S)$ with $T^{S=1}_{\alpha_5\alpha_3\alpha_1\alpha} = (1-\delta_{\alpha\alpha_1})(\delta_{\alpha_3\alpha}\delta_{\alpha_5\alpha_1} - \delta_{\alpha_3\alpha_1}\delta_{\alpha_5\alpha})$, $T^{S=0}_{\alpha_5\alpha_3\alpha_1\alpha} = 2^{(1-\delta_{\alpha\alpha_1})/2}(\delta_{\alpha_3\alpha}\delta_{\alpha_5\alpha_1} + \delta_{\alpha_3\alpha_1}\delta_{\alpha_5\alpha})$, $T_{\sigma_5\sigma_3\sigma_1\sigma}(S=1) = \delta_{\sigma\sigma_1\sigma_3\sigma_5} + (1/2)(1-\delta_{\sigma\sigma_1})(\delta_{\sigma_3\sigma}\delta_{\sigma_5\sigma_1} + \delta_{\sigma_3\sigma_1}\delta_{\sigma_5\sigma})$, and $T_{\sigma_5\sigma_3\sigma_1\sigma}(S=0) = (1/2)(1-\delta_{\sigma\sigma_1})(\delta_{\sigma_3\sigma}\delta_{\sigma_5\sigma_1} - \delta_{\sigma_3\sigma_1}\delta_{\sigma_5\sigma})$. The two-particle operator $d^+_{i\alpha\sigma}d^+_{i\alpha_1\sigma_1} = (1-\delta_{\alpha\alpha_1})\{\varphi^{(\sigma)}_{i\alpha\alpha_1}(S=1) + \varphi^{(\sigma)}_{i\alpha\alpha_1}(S=0)\} + \delta_{\alpha\alpha_1}\varphi^{(\sigma)}_{i\alpha\alpha_1}(S=0)$ appearing in the perturbation procedure when computing the effective Hamiltonian (II.1) can then be expanded according to the $\mathcal{H}_0$ eigenstates. We will conveniently write it under the form,

$$d^+_{i\alpha\sigma}d^+_{i\alpha_1\sigma_1} = \sum_A \left[d^{2+}_{i(\alpha\sigma)(\alpha_1\sigma_1)}\right]^A(S_A), \tag{II.9}$$

where $[d^{2+}_{i(\alpha\sigma)(\alpha_1\sigma_1)}]^A(S_A)$ regroups all contributions characterized by the same energy $2\epsilon_0 + A$ of total spin S_A:

$$\begin{aligned}\mathcal{H}_0\left[d^{2+}_{i(\alpha\sigma)(\alpha_1\sigma_1)}\right]^A(S_A)|\text{vac}\rangle \\ = (2\epsilon_0 + A)\left[d^{2+}_{i(\alpha\sigma)(\alpha_1\sigma_1)}\right]^A(S_A)|\text{vac}\rangle.\end{aligned} \tag{II.10}$$

Here again it is possible to write $d_{i\alpha_5\sigma_5}d_{i\alpha_3\sigma_3}[d^{2+}_{i(\alpha\sigma)(\alpha_1\sigma_1)}]^A(S_A)|\text{vac}\rangle = T^A_{\alpha_5\alpha_3\alpha_1\alpha}(S_A) \times T_{\sigma_5\sigma_3\sigma_1\sigma}(S_A)$ decoupling the orbital part with the spin part.

The spin operator $\mathbf{S_i}$ on site i, and the orbital operators $d^+_{i\beta}d_{i\alpha}$ for $3d$ orbitals α and β on site i being defined in the usual way by the expressions $(\frac{1}{2} + \sigma\cdot\mathbf{S_i})_{\sigma\sigma'} = \sum_\alpha d^+_{i\alpha\sigma'}d_{i\alpha\sigma}$ and $d^+_{i\beta}d_{i\alpha} = \sum_\sigma d^+_{i\beta\sigma}d_{i\alpha\sigma}$, we then have $d^+_{i\beta\sigma'}d_{i\alpha\sigma} = d^+_{i\beta}d_{i\alpha}(\frac{1}{2} + \sigma\cdot\mathbf{S_i})_{\sigma\sigma'}$. Denoting by $\mathbf{q}$ the vector between titanium site i and oxygen site q lying between sites i and j, and defining the energy gap $\Delta_{dn_1} = \epsilon_0 - \epsilon_{n_1} - 5(V - 2K)$, the effective transfer integral from site j, orbital α', to site i, orbital $\alpha_1 (t^{\alpha_1\alpha'}_{ij})^A = \sum_{n_1} t^{n_1\alpha'}_{qj}t^{\alpha_1 n_1}_{iq}/(A + \Delta_{dn_1})$, $\delta_{dn_{12}} = 2\epsilon_0 - (1-\delta_{n_1n_2})(\epsilon_{n_1} + \epsilon_{n_2})$ as well as coefficients:

$$\begin{aligned}\mathcal{F}^{ABC}_{n_4n_3n_2n_1} = {}&\left(\frac{1}{\Delta_{dn_1} + A} + \frac{1}{\Delta_{dn_2} + B}\right) \\ &\times \frac{1}{4\left(\delta_{dn_{12}} + A + B - C\right)} \\ &\times \left(\frac{1}{\Delta_{dn_3} + A} + \frac{1}{\Delta_{dn_4} + B}\right),\end{aligned} \tag{II.11}$$

$$\left[\mathcal{T}^2_{ij}\right]^A_{\alpha_5\alpha_2\alpha'\alpha}(S_A) = \sum_{\alpha_3\alpha_1} T^A_{\alpha_5\alpha_3\alpha_1\alpha}(S_A)\left(t^{\alpha_2\alpha_3}_{ji}\right)^A\left(t^{\alpha_1\alpha'}_{ij}\right)^A, \tag{II.12}$$

$$\left[\mathcal{T}^2_i\right]^A_{\alpha_5n_3n_1\alpha}(S_A) = \sum_{\alpha_3\alpha_1} T^A_{\alpha_5\alpha_3\alpha_1\alpha}(S_A)t^{n_3\alpha_3}_{qi}t^{\alpha_1n_1}_{iq}, \tag{II.13}$$

the expression for the effective Hamiltonian $\mathcal{H}_{\text{eff}}(i-j;\mathbf{q})$ for a pair $i-j$ of titanium ions in the $\mathbf{q}$ direction is given by the contribution of three terms corresponding, respectively, to process (a), (b), and an orbital-only term:

$$\begin{aligned}\mathcal{H}_{\text{eff}}(i-j;\mathbf{q}) = {}&\mathcal{H}^a_{\text{eff}}(i-j;\mathbf{q}) + \mathcal{H}^b_{\text{eff}}(i-j;\mathbf{q}) \\ &+\tilde{\mathcal{H}}_{4,2}(i-j;\mathbf{q}),\end{aligned} \tag{II.14}$$

with

$$\begin{aligned}\mathcal{H}^a_{\text{eff}}(i-j;\mathbf{q}) = {}&\sum_{\alpha_5\alpha_2\alpha'\alpha A}\frac{[\mathcal{T}^2_{ij}]^A_{\alpha_5\alpha_2\alpha'\alpha}(S_A) + [\mathcal{T}^2_{ji}]^A_{\alpha_2\alpha_5\alpha\alpha'}(S_A)}{A} \\ &\times \mathcal{H}^{(S_A)}(\mathbf{S_i},\mathbf{S_j})d^+_{i\alpha_5}d^+_{j\alpha_2}d_{j\alpha'}d_{i\alpha},\end{aligned} \tag{II.15}$$

$$\begin{aligned}\mathcal{H}^b_{\text{eff}}(i-j;\mathbf{q}) = -{}&\sum_{\alpha_in_iABC}\mathcal{F}^{ABC}_{n_4n_3n_2n_1}\left[\mathcal{T}^2_i\right]^A_{\alpha_5n_3n_1\alpha}(S_A) \\ &\times\left[\mathcal{T}^2_j\right]^B_{\alpha_6n_4n_2\alpha'}(S_B)T^C_{n_4n_3n_2n_1}(S_C) \\ &\times\mathcal{H}^{(S_A,S_B,S_C)}(\mathbf{S_i},\mathbf{S_j})d^+_{i\alpha_5}d_{i\alpha}d^+_{j\alpha_6}d_{j\alpha'},\end{aligned} \tag{II.16}$$

$$\begin{aligned}\tilde{\mathcal{H}}_{4,2}(i-j;\mathbf{q}) = {}&\sum_{\alpha_in_iAB}s(S_A)s(S_B)\left[\mathcal{T}^2_i\right]^A_{\alpha_5n_1n_1\alpha}(S_A) \\ &\times\left[\mathcal{T}^2_j\right]^B_{\alpha_6n_2n_2\alpha'}(S_B),\frac{1}{(A+\Delta_{dn_1})(B+\Delta_{dn_2})} \\ &\times\left(\frac{1}{A+\Delta_{dn_1}}+\frac{1}{B+\Delta_{dn_2}}\right)d^+_{i\alpha_5}d_{i\alpha}d^+_{j\alpha_6}d_{j\alpha'}.\end{aligned} \tag{II.17}$$

In these expressions, A,B,C (S_A,S_B,S_C) are representing the Coulombic energies (the total spin) of the two electrons or

TABLE I. $\mathcal{H}^{(S_A)}(\mathbf{S_i},\mathbf{S_j})$ for the different S_A situations.

	$S_A = 1$	$S_A=0$
$\mathcal{H}^{(S_A)}(\mathbf{S_i},\mathbf{S_j})$	$\frac{3}{4} + \mathbf{S_i}\cdot\mathbf{S_j}$	$-\frac{1}{4} + \mathbf{S_i}\cdot\mathbf{S_j}$

two holes intermediate states on site i,j,q, respectively, $s(S_A = 1) = 3/2$, $s(S_A = 0) = -1/2$, $T^C_{n_4 n_3 n_2 n_1}$ is a coefficient (similiar to $T^A_{\alpha_5\alpha_3\alpha_1\alpha}(S_A)$ for the titanium) describing a two-hole oxygen intermediate state while $\mathcal{H}^{(S_A)}(\mathbf{S_i},\mathbf{S_j}) = \sum_{\sigma\sigma'\sigma_1\sigma_2\sigma_3\sigma_5} \delta_{\sigma'\sigma_1}\delta_{\sigma_2\sigma_3} T_{\sigma_5\sigma_3\sigma_1\sigma}(S_A)(\frac{1}{2}+\sigma\cdot\mathbf{S_i})_{\sigma\sigma_5}(\frac{1}{2}+\sigma\cdot\mathbf{S_j})_{\sigma'\sigma_2}$ and $\mathcal{H}^{(S_A,S_B,S_C)}(\mathbf{S_i},\mathbf{S_j}) = 4\sum_{\sigma\sigma'\sigma_1\sigma_{2\sigma_3\sigma_5}} T_{\sigma_5\sigma_3\sigma_1\sigma}(S_A) T_{\sigma_6\sigma_4\sigma_2\sigma'}(S_B)$ $T_{\sigma_4\sigma_3\sigma_2\sigma_1}(S_C)(\frac{1}{2}+\sigma\cdot\mathbf{S_i})_{\sigma\sigma_5}(\frac{1}{2}+\sigma\cdot\mathbf{S_j})_{\sigma'\sigma_6}$ are presented in Tables I and II, respectively.

III. MEAN-FIELD PHASE DIAGRAM

Using the previous expressions, we will now apply the effective Hamiltonian to obtain the mean-field phase diagram. In this aim, let us call (a,b,c,e_1,e_2) the $d_{yz},d_{zx},d_{xy},d_{x^2-y^2},d_{z^2}$ titanium $3d$ orbitals and $(p_{n_a},p_{n_b},p_{n_c})$ the $(2p_y,2p_x,2p_z)$ $2p$ oxygen orbitals when the vector $\mathbf{q}$ between titanium site i and oxygen site q between i and j (as drawn in Fig. 1) is in the $\mathbf{q} = \mathbf{z} = \mathbf{c}$ direction. For a titanium-titanium bond $i - j$ in the $\mathbf{q} = \mathbf{z}$ direction, σ-type hoppings are occurring between orbitals $2p_z$ and d_{z^2}. In the $\mathbf{q} = \mathbf{x}$ and $\mathbf{q} = \mathbf{y}$ directions, σ-type hoppings will happen between ($2p_x$ and d_{x^2}) and ($2p_y$ and d_{y^2}), respectively, favoring each time an AFM state but with a different orbital ordering. A further treatment is thus necessary to determine the crystal spin and orbital ground state for the whole crystal. This problem being extremely difficult to solve, we have used a variational (mean-field) treatment using classical $S = 1/2$ spins and two sublattices A and B to describe the orbital state, wave functions on site $i \in A/B$ being a linear combination of the three t_{2g} orbitals with coefficients $l_{A/B},m_{A/B},n_{A/B}$: $\varphi_i = (l_A a_i^+ + m_A b_i^+ + n_A c_i^+)|\text{vac}\rangle$ and $\varphi_j = (l_B a_j^+ + m_B b_j^+ + n_B c_j^+)|\text{vac}\rangle$ with $l_A^2 + m_A^2 + n_A^2 = l_B^2 + m_B^2 + n_B^2 = 1$. Due to this orbital description, the phase diagram cannot be obtained by just considering the resulting exchange coupling of a single titanium-titanium bond. By optimizing the solutions with respect to these coefficients,[4,36] one can then deduce the phase diagram. The wave function describing the ground state is thus assumed to decouple the spin and orbital degrees of freedom: $\phi = \phi_{\text{orbital}} \times \phi_{\text{spin}}$. This assumption is very bad in one-dimensional systems[37] but can turn to be acceptable in three dimensions to provide (at least) a qualitative picture of the phase diagram. And even if an exact result shows that there is no long-range spin ordering in the KK Hamiltonian,[38] this result is only valid in the original KK model, the addition of perturbations like Hund's rule coupling allowing long-range ordering.[39] In this frame, the (classical) spin state $\phi_{\text{spin}} = (\sigma_1,\sigma_2,\ldots,\sigma_k,\ldots)$ (where $\sigma_k = \pm 1/2$ is the classical spin on site k) is characterized by a wave vector $\mathbf{k}_{\text{spin}} = \mathbf{0}$ for the FM state and $\mathbf{k}_{\text{spin}} = (0,0,\pi),(\pi,\pi,0),\pi = (\pi,\pi,\pi)$ for the A-AFM, C-AFM, and G-AFM states. Therefore $< \mathbf{S_i}\cdot\mathbf{S_j} >= \pm 1/4$ according to the case. The orbital state $\phi_{\text{orb}} = \prod_{(\text{site } i)} \varphi_i$ is also characterized by a wave vector $\mathbf{k}_{\text{orb.}} = \mathbf{0}$ for the ferro-orbital (FO) state and $\mathbf{k}_{\text{orb.}} = (0,0,\pi),(\pi,\pi,0),\pi = (\pi,\pi,\pi)$ for the antiferro-orbital A-AFO, C-AFO, and G-AFO states with two sublattices A and B. In each case, the computed energy $\mathcal{E}[\mathbf{k}_{\text{orb.}},\mathbf{k}_{\text{spin}}](l_A,m_A,n_A,l_B,m_B,n_B) =< \phi|(1/2)\sum_{ij\mathbf{q}} \mathcal{H}_{\text{eff}}(i-j,\mathbf{q})|\phi >$ must be optimized as respect to parameters l_A,m_A,n_A,l_B,m_B,n_B. Due to the great number of parameters, the optimization is rather difficult. Two cases are generally exactly solvable: the case ($\mathbf{k}_{\mathbf{orb.}} = \mathbf{0}; \mathbf{k}_{\mathbf{spin}} = \mathbf{0} or \pi$) and the case ($\mathbf{k}_{\mathbf{orb.}} = \pi; \mathbf{k}_{\mathbf{spin}} = \mathbf{0} or \pi$). In this last case (lower in energy), the optimization leads to the relation $l_A l_B = m_A m_B = n_A n_B = 0$ [for instance, ($l_A = 1, m_A = 0, n_A = 0, l_B = 0, m_B = cos\theta, n_B = sin\theta$) fulfill this condition]. A numerical study shows that the G-AFO states are the lowest in energy except in the case of high degeneracy occurring when the Racah parameter $\mathcal{B}$ tends to zero. The distinction between G-AFM, C-AFM, A-AFM, and FM states being also difficult to achieve, we have tested a subset of possible states and drawn the phase diagram considering a G-AFO ground state with the conditions ($l_A = 1, m_A = 0, n_A = 0, l_B = 0, m_B = 1, n_B = 0$) for the G-AFM, C-AFM, and FM states, and ($l_A = 1, m_A = 0, n_A = 0, l_B = 0, m_B = 0, n_B = 1$) for the A-AFM state, these conditions (or equivalent one) giving apparently the lowest possible energy in each case. Under such a condition, the phase diagram is presented in Fig. 4 as a function of some of the parameters appearing in the problem. The G/C-AFM magnetic states are favored by small values of t_π/t_σ, Δ_0 and high values of Δ^{oxy}_{zx}, $\mathcal{A}$, $\mathcal{B}$ and $V - 2K$. Using the expected value $t_\pi/t_\sigma \sim 0.5$, the $RTiO3$ model sits in the FM phase, close to the line separating ferromagnets from antiferromagnets.

IV. SPIN-ORBIT COUPLING

If we now introduce the spin-orbit coupling, the Hamiltonian becomes: $\mathcal{H}_{\text{eff}}(i-j,\mathbf{q},\lambda) = \mathcal{H}_{\text{eff}}(i-j,\mathbf{q}) + \lambda(\mathbf{l_i}\cdot\mathbf{S_i} + \mathbf{l_j}\cdot\mathbf{S_j})$ where $\mathbf{l_i} = \mathcal{P}_{t_{2g}}\mathbf{L_i}\mathcal{P}_{t_{2g}}$ is the projection on the t_{2g} subspace of the full orbital momentum $\mathbf{L_i}$ of the $3d$ electron site i. The ground state resulting from the numerical diagonalization of $\mathcal{H}_{\text{eff}}(i-j,\mathbf{q},\lambda)$ for a one-bond i-j system contains both a ferromagnetic and an antiferromagnetic wave function whose

TABLE II. Summation results over spin indices for process (b) according to the different S_A,S_B,S_C situations [here, $\epsilon(1) = -1$ and $\epsilon(0) = 1$].

(S_A,S_B,S_C)	(1,1,1)	(1,1,0) (1,0,1) (0,1,1)	(1,0,0) (0,1,0) (0,0,1)	(0,0,0)
$\mathcal{H}^{(A,B,C)}(\mathbf{S_i},\mathbf{S_j})$	$6 + \frac{3}{4} + \mathbf{S_i}\cdot\mathbf{S_j}$	$\epsilon(S_C)(2 + \frac{1}{4} - \mathbf{S_i}\cdot\mathbf{S_j})$	$-\epsilon(S_C)(\frac{3}{4} + \mathbf{S_i}\cdot\mathbf{S_j})$	$\frac{1}{4} - \mathbf{S_i}\cdot\mathbf{S_j}$

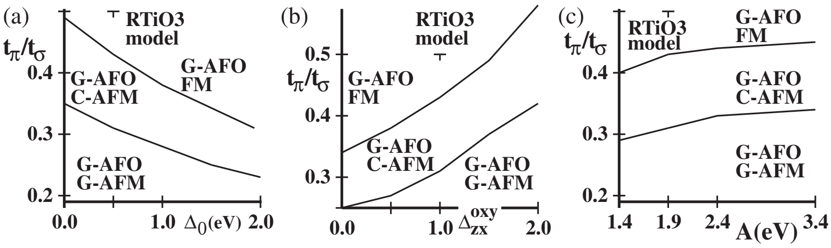

FIG. 4. (a) Mean-field phase diagram in the $(\Delta_0, t_\pi/t_\sigma)$ plane. (b) Mean-field phase diagram in the $(\Delta zx^{oxy}, t_\pi/t_\sigma)$ plane. (c) Mean-field phase diagram in the $(\mathcal{A}, t_\pi/t_\sigma)$ plane (here, $\mathcal{A} = U - 1.6$ eV).

amplitudes are t_π/t_σ dependent. Therefore, let us consider the most simple solution of this kind for the whole crystal (with only one parameter) by defining

$$\text{for site } i \in A: \psi_i = A_1\alpha^+_{i\uparrow} + A_2\beta^+_{i\downarrow}, \tag{IV.1}$$

$$\text{for site } j \in B: \psi_j = \gamma^+_{j\downarrow}, \tag{IV.2}$$

with α,β,γ belonging to the t_{2g} manifold a,b,c. Then, the two-particle state $\psi_i\psi_j = A_1\alpha^+_{i\uparrow}\gamma^+_{j\downarrow} + A_2\beta^+_{i\downarrow}\gamma^+_{j\downarrow}$ mixes an FM state together with a (G-)AFM one. In order for A_1 and A_2 to be nonzero simultaneously, the spin orbit coupling must lower the energy of the system. If we consider the case $\alpha = b$ and $\beta = c$, as $\langle \mathbf{l_i} \cdot \mathbf{S_i} \rangle_{\psi_i} = \mathrm{Re}(iA_1^*A_2)$ we can choose $\psi_i = A_\lambda(t_\pi/t_\sigma)b^+_{i\uparrow} + iB_\lambda(t_\pi/t_\sigma)c^+_{i\downarrow}$ with $A_\lambda(t_\pi/t_\sigma), B_\lambda(t_\pi/t_\sigma)$ positive real numbers obeying $A^2_\lambda(t_\pi/t_\sigma) + B^2_\lambda(t_\pi/t_\sigma) = 1$. In such a case, $\langle \mathbf{l_i} \cdot \mathbf{S_i} \rangle_{\psi_i} = -A_\lambda(t_\pi/t_\sigma)B_\lambda(t_\pi/t_\sigma)$ is negative, $\langle \mathbf{S_i} \cdot \mathbf{S_j} \rangle_{\psi_i\psi_j} = (B^2_\lambda(t_\pi/t_\sigma) - A^2_\lambda(t_\pi/t_\sigma))/4$ while $A_\lambda(t_\pi/t_\sigma)$ is obtained by minimizing the energy of the system. The energy per site is plotted on Fig. 5 before and after the transition G-AFM/FM for different λ values, $A_\lambda(t_\pi/t_\sigma)$ corresponding to the value minimizing the energy of the system and lying in the range [0,1]. When $\lambda = 0$, $\psi_j = a^+_{j\downarrow}$ gives the lowest energy (G-AFO state) with $A_\lambda(t_\pi/t_\sigma) = 1$ when t_π/t_σ is in the G-AFM part of the phase diagram and with $A_\lambda(t_\pi/t_\sigma) = 0$ when t_π/t_σ is in the FM part of the phase diagram, as expected. When $\lambda \neq 0$, $A_\lambda(t_\pi/t_\sigma)$ is now lying in the range]0,1[. In Fig. 6 we have plotted $\langle \mathbf{S_i} \cdot \mathbf{S_j} \rangle_{\psi_i\psi_j}$ and $\langle \mathbf{l_i} \cdot \mathbf{S_i} \rangle_{\psi_i}$ as a function of t_π/t_σ at $\lambda = 0$ and $\lambda = 20$ meV; thanks to the spin-orbit coupling, $\langle \mathbf{S_i} \cdot \mathbf{S_j} \rangle_{\psi_i\psi_j}$ passes continuously from $-1/4$ to $+1/4$. Consequently, if the system lies in the G-AFM part of the diagram close to the line separating G-AFM to FM, its magnetic parameter value will be extremely reduced and it will also present a weak ferromagnetic moment. But when the system is in the FM part not too close to the transition, the value of the magnetic parameter will be closed to the one obtained without the spin-orbit coupling.

V. SUMMARY

In this article, we have derived an effective spin-orbital Hamiltonian for $3d^1$ electronic systems with t_{2g} orbital degeneracy. This derivation was done up to order four in the hopping term, without any approximations concerning the Coulombic interactions. From this study, we see that the participation of the oxygen and of the e_g levels gives rise to the σ-type electron hopping which cannot be mapped onto an effective M-M bond and favors the emergence of an AFM ground state (of G or C type as predicted by the classical treatment) in competition with an FM one. This therefore greatly improves the preceding KK Hamiltonian essentially predicting ferromagnetism in the ideal cubic case.[4] The stability of these phases is driven by several parameters and we have obtained that small values for $t_\pi/t_\sigma, \Delta_0, \epsilon_d - \epsilon_n$ and large values for $\Delta_{zx}^{oxy}, \mathcal{A}, \mathcal{B}$, and $V - 2K$ are favoring the AFM phases. Using the expected value $t_\pi/t_\sigma \sim 0.5$,[19] we have placed our $RTiO_3$ model (assuming an ideal cubic system) on the phase diagrams which sits in the FM phase, close to the line separating ferromagnets from antiferromagnets. In any case, it is clear from this study that σ-type electron hoppings cannot be neglected when studying $3d^n$ ($n = 1,2,3$) RMO_3 systems: for $3d^3$ and $3d^2$ systems like $LaCrO_3$, $LaVO_3$, and YVO_3 which are either G-AFM or C-AFM, the omission of this process only leads to a bad quantitative description, but it turns out to be

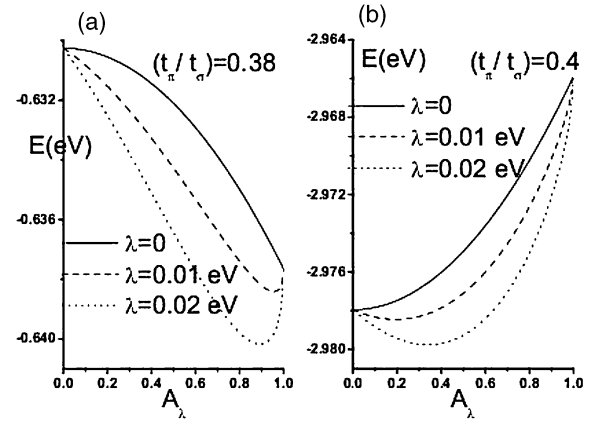

FIG. 5. λ dependence of parameter $A_\lambda(t_\pi/t_\sigma)$ corresponding to the minimum of the energy per site. (a) Before the critical value; (b) after the critical value.

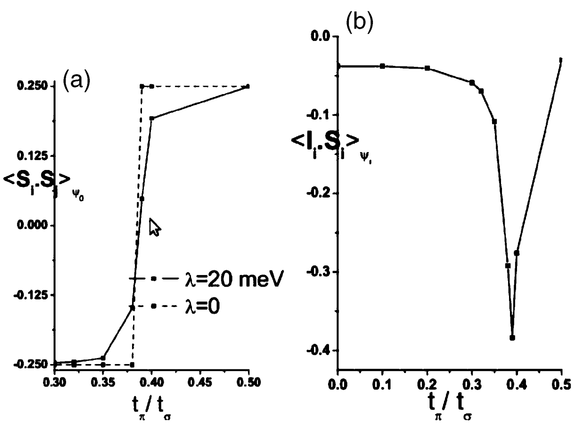

FIG. 6. (a) $\langle \mathbf{S_i} \cdot \mathbf{S_j} \rangle_{\psi_i\psi_j}$ for $\lambda = 0$ and $\lambda = 20$ meV. (b) $\langle \mathbf{l_i} \cdot \mathbf{S_i} \rangle_{\psi_i}$ for $\lambda = 20$ meV as a function of t_π/t_σ.

worse for $3d^1$ compounds as the possibility to obtain AFM is greatly reduced. In this last case, due to the great number of parameters involved in our model, it is plausible to expect that a more precise description of the parameters describing $LaTiO_3$ (assuming this system has very small distortions) also improved by a description in terms of the orbital-liquid state; on the other hand the presence of a pronounced $GdFeO_3$-type lattice distortion (characterized by the Ti-O-Ti angle θ) in $YTiO_3$ lowering the amplitude of the σ-type AFM process ($t_{iq}^{d_{z^2}2p_z} = -t_\sigma \cos\theta$) will be effective in distinguishing $LaTiO_3$ from $YTiO_3$, shifting the former into being AFM. In such a case, the spin-orbit coupling which has been shown to allow a continuous transition of $\langle \mathbf{S_i} \cdot \mathbf{S_j} \rangle_{\psi_i \psi_j}$ from $-1/4$ to $+1/4$ as a function of t_π / t_σ would help to explain the small value of the ordered parameter reported for $LaTiO_3$ as well as its weak ferromagnetic moment. Another improvement of the model would be to introduce the delocalization of the one- and two-electron hole intermediate states, as hole delocalizations are always stabilizing the system. A description of the oxygen orbitals similar to the one done in the case of a Zhang-Rice singlet[40] could thus be done both for the singlet and for the triplet intermediate hopping states.

ACKNOWLEDGMENTS

This research was supported by grants from the US-Israel Binational Science Foundation and from the German-Israeli Foundation.

---

[1] J. Goodenough, Phys. Rev. **100**, 564 (1955).

[2] K. Kugel and D. Khomskii, Sov. Phys. Solid State **17**, 285 (1975).

[3] S. Ishihara, J. Inoue, and S. Maekawa, Phys. Rev. B **55**, 8280 (1997).

[4] S. Ishihara, T. Hatakeyama, and S. Maekawa, Phys. Rev. B **65**, 064442 (2002).

[5] M. Mochizuki and M. Imada, J. Phys. Soc. Jpn. **70**, 1777 (2001).

[6] G. Khaliullin and S. Maekawa, Phys. Rev. Lett. **85**, 3950 (2000).

[7] G. Khaliullin and S. Okamoto, Phys. Rev. Lett. **89**, 167201 (2002).

[8] A. M. Oles, P. Horsch, L. F. Feiner, and G. Khaliullin, Phys. Rev. Lett. **96**, 147205 (2006).

[9] D. A. MacLean, H.-N. Ng, and J. E. Greedan, J. Solid State Chem. **30**, 35 (1979).

[10] B. Keimer, D. Casa, A. Ivanov, J.W. Lynn, M.V. Zimmermann, J. P. Hill, D. Gibbs, Y. Taguchi, and Y. Tokura, Phys. Rev. Lett. **85**, 3946 (2000).

[11] G. Khaliullin, Phys. Rev. B **64**, 212405 (2001).

[12] G. Khaliullin and S. Okamoto, Phys. Rev. B **68**, 205109 (2003).

[13] G. Khaliullin, Prog. Theor. Phys. Suppl. **160**, 155 (2005).

[14] M. Mochizuki and M. Imada, J. Phys. Soc. Jpn. **70**, 2872 (2001).

[15] M. Mochizuki and M. Imada, Phys. Rev. Lett. **91**, 167203 (2003).

[16] C. Ulrich, G. Khaliullin, S. Okamoto, M. Reehuis, A. Ivanov, H. He, Y. Taguchi, Y. Tokura, and B. Keimer, Phys. Rev. Lett. **89**, 167202 (2002).

[17] M. Cwik, T. Lorenz, J. Baier, R. Muller, G. Andre, F. Bouree, F. Lichtenberg, A. Freimuth, R. Schmitz, E. Muller-Hartmann *et al.*, Phys. Rev. B **68**, 060401 (2003).

[18] M. W. Haverkort *et al.*, Phys. Rev. Lett. **94**, 056401 (2005).

[19] R. Schmitz, O. Entin-Wohlman, A. Aharony, A. B. Harris, and E. Muller-Hartmann, Phys. Rev. B **71**, 144412 (2005).

[20] I. V. Solovyev, Phys. Rev. B **74**, 054412 (2006).

[21] T. Kiyama *et al.*, Physica B **329–333**, 733 (2003).

[22] S. Streltsov *et al.*, Phys. Rev. B **71**, 245114 (2005).

[23] A. Mozhegorov *et al.*, Phys. Solid State **50**, 1795 (2008).

[24] J. Slater and G. Koster, Phys. Rev. **94**, 1498 (1954).

[25] F. de Groot *et al.*, Phys. Rev. B **40**, 5715 (1989).

[26] T. Mizokawa and A. Fujimori, Phys. Rev. B **54**, 5368 (1996).

[27] L. Mattheiss, Phys. Rev. B **6**, 4718 (1972).

[28] J. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, Cambridge, 1961).

[29] P. Mahadevan, N. Shanthi, and D. Sarma, Phys. Rev. B **54**, 11199 (1996).

[30] A. Bocquet, T. Mizokawa, K. Morikawa, A. Fujimori, S. Barman, D. S. K. Mati, Y. Tokura, and M. Onoda, Phys. Rev. B **53**, 1161 (1996).

[31] T. Arima, Y. Tokura, and J. Torrance, Phys. Rev. B **48**, 17006 (1993).

[32] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Oxford University Press, New York, 1970).

[33] C. Bloch, Nucl. Phys. **6**, 329 (1958).

[34] J. des Cloizeaux, Nucl. Phys. **20**, 321 (1960).

[35] I. de P. R Moreira, N. Suaud, N. Guihery, J. Malrieu, R. Caballol, J. Bofill, and F. Illas, Phys. Rev. B **66**, 134430 (2002).

[36] A. M. Oles, L. F. Feiner, and J. Zaanen, Phys. Rev. B **61**, 6257 (2000).

[37] B. Frischmuth, F. Mila, and M. Troyer, Phys. Rev. Lett. **82**, 835 (1999).

[38] A. Harris, T. Yildirim, A. Aharony, O. Entin-Wohlman, and I. Korenblit, Phys. Rev. Lett. **91**, 087206 (2003).

[39] A. Harris, A. Aharony, O. Entin-Wohlman, I. Korenblit, and T. Yildrim, Phys. Rev. B **69**, 094409 (2004).

[40] F. Zhang and T. Rice, Phys. Rev. B **37**, 3759 (1988).