Weak ferromagnetism in the low-temperature tetragonal phase of the cuprates

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The criterion for the existence of weak ferromagnetism in the low-temperature distorted phases of La_2CuO_4-type compounds is derived on the basis of a general superexchange Hamiltonian. It is found that a ferromagnetic canting out of the CuO_2 planes is *excluded* in the pure low-temperature tetragonal phase. The anisotropic superexchange interactions between the copper spins are obtained from a Hubbard model which includes all copper 3d and oxygen 2p orbitals, and all on–site Coulomb matrix elements. The results apply when the oxygen octahedra surrounding each copper have tetragonal symmetry. Explicit expressions for the net ferromagnetic moment and the in-plane and the out-of-plane gaps in the spin-wave spectrum are derived and estimated in terms of the microscopic parameters of the cuprates.

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I. INTRODUCTION

The magnetic anisotropies of La_2CuO_4-type compounds have attracted considerable attention in recent years. These materials are antiferromagnets, with a dominant easy-plane anisotropy.[1] In the orthorhombic phase of La_2CuO_4, the oxygen octahedra surrounding each copper ion rotate by a small angle relative to their location in the tetragonal phase. The structural distortion together with the spin-orbit interaction on the transition metal ions allows for the appearance of the antisymmetric Dzyaloshinskii-Moriya interaction.[2] This may cause a net ferromagnetic moment perpendicular to the CuO_2 plane.[3–5] The possibility of a small out-of-plane canting of the antiferromagnetically ordered Cu spins depends in a subtle way on the crystal symmetry. Its actual existence in the low-temperature tetragonal (LTT) phase is still debated in the literature.[6–9]

Of particular interest in this respect is the doped $La_{2-x}Nd_xCuO_4$ system, in which the direction of the tilting axis of the octahedra depends on the temperature and on the dopant concentration.[10] Here, the CuO_6 octahedra rotate around a general axis in the basal plane of the high-temperature tetragonal (HTT) phase, which makes an angle $\pi/4-\alpha$ with the $\hat{a}-$axis (or an angle α with the $\hat{x}-$axis, see Fig. 1). In particular, α is equal to zero in the LTT phase, α equals $\pi/4$ in the low-temperature orthorhombic (LTO) phase (sometimes denoted LTO1 phase), and α interpolates between these two values in the LTO2 phase. Previous calculations by Bonesteel[7] and Entin-Wohlman *et al.*[11] have predicted that the ferromagnetic moment of each copper-oxide layer decreases with α, reaching zero in the LTT phase, while Koshibae *et al.*[8,9] argue that the canted moments remain finite. Experimentally[3–5] one finds a weak ferromagnetic moment in the LTO2 phase which seems to persist in the vicinity of the LTT phase. However, this may be attributed to the magnetic moment of the Nd ions.

In general, the magnetic anisotropies are analyzed on the basis of Anderson's theory[12] of kinetic superexchange and Moriya's extension[13] to incorporate spin-orbit interactions. The application of these theories to the CuO_2 plane has been first attempted by Coffey, Bedell, and Trugman[14] and Coffey, Rice, and Zhang[15] who have concentrated on the antisymmetric Dzyaloshinskii-Moriya anisotropy, but have not included the symmetric anisotropy contributions. However, as has been shown by Shekhtman *et al.*,[16] the symmetric anisotropies can never be neglected, since their contribution to the magnetic energy is of the same order of magnitude as that of the antisymmetric anisotropy. Consequently, Bonesteel,[7] Shekhtman *et al.*,[6] and Koshibae *et al.*[8,9] have presented expressions for the magnetic Hamiltonian which includes both types of anisotropies.

All these studies are based on terms requiring the existence of a structural distortion. As a result, they produce magnetic anisotropies which vanish in the pure tetragonal symmetry. However, tetragonal systems isostructural to La_2CuO_4, like $Sr_2CuO_2Cl_2$,[17] Nd_2CuO_4[18], and Pr_2CuO_4[19], which do not undergo a structural distortion, show an uniaxial spin anisotropy that is of the same order of magnitude as in the orthorhombic phase of La_2CuO_4. It is thus clear that some important ingredients are missing in the previous calculations. Recently, it has been shown by Yildirim *et al.*[20] that symmetric magnetic anisotropies arise in the tetragonal phase when Moriya's theory is extended to include (i) hopping between excited states on the copper and oxygen ions, and (ii) Coulomb exchange interactions whose matrix elements depend on the orbitals. This scheme has been extended[21] to include the most general on–site Coulomb interactions (including those which involve more than two orbitals) when two holes occupy the same site. The resulting Hamiltonian[21] applies when the oxygen ions surrounding the copper sites form a rotated octahedron which has tetragonal symmetry. In this paper we use these results to derive the magnetic interactions between a nearest neighbor pair of copper ions in the CuO_2 plane for the case of a general tilting axis of the oxygen octahedra. We obtain an explicit expression for the weak ferromagnetic moment of the plane. When this moment is normalized by its value in the LTO phase, we find that it depends only on the orientation of the tilting axis and on a single parameter which absorbs all the coupling constants of the spin Hamiltonian. We derive a criterion for the existence of weak ferromagnetism in the LTT phase and analyze it in terms of realistic cuprate parameters. It is found that this criterion excludes the possibility of a weak ferromagnetic moment in the LTT phase due to kinetic superexchange, contrary to the claim of Koshibae *et al.*.[9]

To complete the analysis of the magnetic couplings due to general Coulomb interactions, one should also include the anisotropies generated by the direct exchange mechanism, involving *nonlocal* Coulomb matrix elements. The effect of nonlocal Coulomb interactions with general matrix elements has already been studied in detail,[22] showing that the direct exchange only leads to anisotropies which are not qualitatively different from those generated by kinetic superexchange and generally can be neglected as small. Therefore, in the derivation of the magnetic Hamiltonian we do not consider contributions from nonlocal Coulomb interactions.

The paper is organized as follows: The magnetic order in the ground state of the copper spin Hamiltonian is analyzed in section II. We show that the ferromagnetic canting of the spins is not possible in the LTT phase, and that the claim of Koshibae *et al.* is based on erroneous assumptions concerning the values of the microscopic cuprate parameters. In section III we derive the spin-wave gaps and find the splitting of the in-plane and out-of-plane components. In order to make the paper self-contained, we present in section IV the derivation of the effective magnetic interactions from the microscopic Hamiltonian. This is accomplished by a perturbation expansion around the half-filled ground state, which includes hopping between all orbital states of two neighboring copper and oxygen ions, and the complete on–site Coulomb interaction. Thus our derivation encompasses processes disregarded in previous works. In section V we describe the computations of the various magnetic couplings. Finally, section VI contains a summary and a critical discussion of our results.

II. THE GROUND STATE CONFIGURATION OF THE MAGNETIC HAMILTONIAN AND WEAK FERROMAGNETISM

Within the theory of kinetic superexchange, one derives an effective magnetic Hamiltonian for the Cu spins by treating perturbatively the Hubbard Hamiltonian of a single Cu-O-Cu bond around the half-filled ground state, in which there is one hole on each Cu-ion. This way one obtains the magnetic interaction between two neighboring copper ions. These interactions are then added together on the four bonds constituting the elementary plaquette of the CuO_2 plane (see Fig. 1), with the assumption that the copper lattice is divided into two interpenetrating sublattices with magnetizations $\mathbf{M}_1$ and $\mathbf{M}_2$. The detailed calculations are given in sections IV and V. The result for the effective magnetic Hamiltonian of the plaquette, normalized by the number of bonds, can be written in the form

$$\mathcal{H} = J\mathbf{M}_1 \cdot \mathbf{M}_2 + \mathbf{D} \cdot (\mathbf{M}_1 \times \mathbf{M}_2) + \mathbf{M}_1 \boldsymbol{\Gamma} \mathbf{M}_2. \qquad (1)$$

Here the vector $\mathbf{D}$ is directed along the rotation axis of the oxygen octahedra, $\hat{n}$,

$$\mathbf{D} = D\hat{n},\ \hat{n} = \hat{x}\cos\alpha + \hat{y}\sin\alpha, \qquad (2)$$

where the unit vectors $\hat{x}$ and $\hat{y}$ lie in the CuO_2 plane (see Fig. 1), and the symmetric tensor $\boldsymbol{\Gamma}$ is given by

$$\boldsymbol{\Gamma} = \begin{pmatrix} \Gamma\cos^2\alpha & \Gamma_2\sin\alpha\cos\alpha & 0 \\ \Gamma_2\sin\alpha\cos\alpha & \Gamma\sin^2\alpha & 0 \\ 0 & 0 & \Gamma_z \end{pmatrix}. \qquad (3)$$

As mentioned, the magnetic interactions are obtained from the microscopic Hamiltonian of the Cu-O-Cu bond by a perturbation expansion. This yields that J [Eqs. (42) below] is the leading coupling, of order t_0^4, where t_0 is the matrix element for hopping between the ground state orbitals of neighboring copper and oxygen ions. The other coupling parameters are generated by the spin-orbit interaction on the copper, and therefore are smaller. Denoting the spin-orbit coupling strength by λ, one finds that to leading order [see Eqs. (42)] the antisymmetric anisotropy D is proportional to $t_0^4\lambda\delta$, where δ is the small angle of tilting of the oxygen octahedra around the axis $\hat{n}$, and $\Gamma \sim t_0^4\lambda^2\delta^2$ [*cf.* Eqs. (42)]. The previous studies of the magnetic Hamiltonian[7–9,11] have included only these three parameters and therefore have yielded an isotropic magnetic interaction in the undistorted HTT phase for which $\delta = 0$. This results from the neglect of various Coulomb interactions.[20,21] These are included in the present calculation. As a result, one finds that $\Gamma_2 \sim t_0^4\lambda^2\delta^2 K$ [Eq. (47)], and $\Gamma_z \sim t_0^4\lambda^2 K$ [Eq. (48)]. Here K stands for the order of magnitude of the Coulomb matrix elements. These in general are different for different orbitals. We omit this dependence here (but not in the full calculation, see Secs. IV and V) for convenience. One notes that the out-of-plane anisotropy represented by Γ_z persists also in the pure tetragonal phase. Although the coupling constants of the magnetic Hamiltonian are evaluated to leading orders in the spin-orbit interaction, we find that the results (2) and (3) are valid to *all* orders in λ.

We now analyze the classical magnetic ground state configuration pertaining to the interaction (1). To this end, we first eliminate the antisymmetric anisotropy by performing an alternate rotation of the coordinate system on the two sublattices around the axis $\hat{n}$ by a small angle $\pm\theta$. This angle is chosen such that the magnetic interaction will be symmetric to order $\lambda^2\delta^2$. The transformed sublattice magnetizations, $\mathbf{M}_1'$ and $\mathbf{M}_2'$, are given by

$$\mathbf{M}_{1,2} = \mathbf{M}_{1,2}'\cos\theta + \hat{n}(\hat{n}\cdot\mathbf{M}_{1,2}')(1-\cos\theta) \\ \pm \mathbf{M}_{1,2}'\times\hat{n}\sin\theta,\ \tan 2\theta = D/J. \tag{4}$$

The transformed magnetic Hamiltonian then becomes

$$\mathcal{H}' = \left(J + \frac{D^2}{2J}\right)\mathbf{M}_1'\cdot\mathbf{M}_2' + \mathbf{M}_1'\mathbf{\Gamma}'\mathbf{M}_2', \tag{5}$$

with the new symmetric anisotropy tensor

$$\begin{aligned}\mathbf{\Gamma}' = &\left(\Gamma - \frac{D^2}{2J}\right)\hat{n}\otimes\hat{n} + \Gamma_z\hat{z}\otimes\hat{z} \\ &- \frac{1}{2}(\Gamma-\Gamma_2)\Big(\sin^2 2\alpha(\hat{n}\otimes\hat{n} - \hat{n}_\perp\otimes\hat{n}_\perp) \\ &+ \frac{1}{2}\sin 4\alpha(\hat{n}\otimes\hat{n}_\perp + \hat{n}_\perp\otimes\hat{n})\Big),\end{aligned} \tag{6}$$

where $\hat{n}_\perp$ is a unit vector perpendicular to $\hat{n}$,

$$\hat{n}_\perp = -\hat{x}\sin\alpha + \hat{y}\cos\alpha. \tag{7}$$

It is now straightforward to diagonalize $\mathcal{H}'$, keeping terms up to order $\lambda^2\delta^2$. One finds

$$\mathcal{H}' = \mathbf{M}_1'(\Lambda_+\hat{e}_+\otimes\hat{e}_+ + \Lambda_-\hat{e}_-\otimes\hat{e}_- + \Lambda_z\hat{z}\otimes\hat{z})\mathbf{M}_2', \tag{8}$$

with the eigenvalues

$$\begin{aligned}\Lambda_z &= J + \frac{D^2}{2J} + \Gamma_z, \\ \Lambda_\pm &= J + \Gamma + \frac{\Gamma-\Gamma_2}{4(1-\Omega)} \\ &\times\left(2\Omega - 1 \pm\sqrt{1-4\Omega(1-\Omega)\cos^2 2\alpha}\right).\end{aligned} \tag{9}$$

Here we have introduced the dimensionless parameter

$$\Omega = 1 - \frac{1}{2}(\Gamma-\Gamma_2)\left(\frac{D^2}{2J} - \Gamma_2\right)^{-1}. \tag{10}$$

The criterion for weak ferromagnetism will be given in terms of Ω alone. The eigenvectors of the Hamiltonian $\mathcal{H}'$ are $\hat{z}$, which corresponds to the out-of-plane anisotropy Λ_z, and the two in-plane eigenvectors

$$\begin{aligned}\hat{e}_+ &= \hat{n}\cos\phi - \hat{n}_\perp\sin\phi, \\ \hat{e}_- &= \hat{n}\sin\phi + \hat{n}_\perp\cos\phi,\end{aligned} \tag{11}$$

with

$$\tan 2\phi = \frac{\sin 4\alpha}{\cos 4\alpha - \Omega(1-\Omega)^{-1}}. \tag{12}$$

Inspection of (12) reveals that as long as $\Omega < \frac{1}{2}$ the angle ϕ increases from 0 to $\pi/2$ as α grows from 0 to $\pi/4$, that is, as the rotation axis of the octahedron tilts toward the $\hat{a}$-axis. On the other hand, for $\Omega > \frac{1}{2}$ the dependence of ϕ on α is nonmonotonic, starting with $\phi = \pi/2$ for $\alpha = 0$, decreasing as α increases, going through a minimum and then reaching $\pi/2$ as $\alpha \to \pi/4$. As we shall see, these properties determine the dependence of the ferromagnetic moment on the direction of the tilting axis.

Our numerical evaluations of the spin coupling parameters show that $\Lambda_+ > \Lambda_- > \Lambda_z$, and therefore the Hamiltonian (5) is minimized when $\mathbf{M}_1' = -\mathbf{M}_2'$ points along $\hat{e}_+$. Substituting this into (4) gives that the orientation of the magnetic moments in the ground state, to leading order in δ, is

$$\frac{\mathbf{M}_{1,2}}{S} = \pm(\hat{n}\cos\phi - \hat{n}_\perp\sin\phi\cos\theta) + \hat{z}\sin\phi\sin\theta. \tag{13}$$

Hence there is a staggered in-plane ordering of the spins along the axis $\hat{x}\cos(\alpha-\eta) + \hat{y}\sin(\alpha-\eta)$ with $\tan\eta = \tan\phi\cos\theta$ and a small (of order δ) ferromagnetic moment $\mathbf{M}_F = S\hat{z}\sin\phi\sin\theta$ perpendicular to the plane. The magnitude of the ferromagnetic moment, $M_F(\alpha)$, as function of the direction of the tilting axis is given by

$$\left(\frac{M_F(\alpha)}{SD/2J}\right)^2 = \frac{1}{2}\left(1 + \frac{1-2(1-\Omega)\cos^2 2\alpha}{(1-4\Omega(1-\Omega)\cos^2 2\alpha)^{1/2}}\right) \tag{14}$$

and is depicted in Fig. 2 for several values of Ω.

Surprisingly, the expression (14) is identical to the result obtained for M_F in Ref. 11, which considered only orbital-independent direct Coulomb terms on the coppers. However, in the present work the parameter Ω is more general and contains Γ_2 as an additional magnetic coupling constant. When $\Omega = 0$, the simple relation $M_F(\alpha) = SD/2J\sin 2\alpha$ is recovered.[7] The expression (14) for M_F is valid in the entire range of $\Omega < 1$ and gives $M_F(\pi/4) = SD/2J$ in the LTO phase. In the LTT phase, it leads to $M_F(0) = 0$ for $\Omega < \frac{1}{2}$, whereas $M_F(0) = SD/2J$ for $\Omega > \frac{1}{2}$. The condition for a non-vanishing weak ferromagnetic moment in the LTT phase therefore reads

$$\Omega > \frac{1}{2} \quad \text{or} \quad \Gamma - \frac{D^2}{2J} < 0. \tag{15}$$

This generalizes the inequality derived by Koshibae *et al.*[9] in the framework of kinetic superexchange, including orbital-independent Coulomb interactions, but not Coulomb exchange terms and general Coulomb matrix elements. Remarkably, the microscopic hopping integrals, t_0, the spin-orbit coupling constant, λ, and the tilting angle of the CuO_6 octahedra, δ, drop out from the parameter Ω which is determined only by the various local one- and two-hole energies (see Secs. IV and V). Also the in-plane-anisotropy Γ_2 does not enter the condition (15).

Using the expressions (42) for the magnetic coupling constants, the criterion for weak ferromagnetism in the LTT phase can be expressed in terms of the orbital energies on the oxygen and the Coulomb parameters alone. With the notation of Eq. (33), we find the condition

$$\frac{g_{p_\sigma p_\sigma}(g_{p_\sigma p_\sigma}+g_{p_z p_z}+2g_{p_\sigma p_z})}{(g_{p_\sigma p_\sigma}+g_{p_\sigma p_z})^2}<\frac{1}{2}. \quad (16)$$

To evaluate this criterion, we have used the Racah parameters[23] $A = 7.0$ eV, $B = 0.15$ eV, $C = 0.58$ eV for the Coulomb terms on the copper, and for the oxygen we have chosen[24,25] the Slater-Condon parameters $F_0 = 3.1$ eV and $F_2 = 0.28$ eV. The orbital energies of the oxygen[24–26] are taken as $\epsilon_{p_\sigma} = 3$ eV and $\epsilon_{p_\pi} = \epsilon_{p_z} = 2$ eV. For these parameters the value 0.88 for the l.h.s. of (16) is obtained, excluding the possibility of a weak ferromagnetic moment in the pure low-temperature-tetragonal symmetry. A strong dependence of the quantities entering this criterion on the oxygen energies is found, which are, however, bounded by[24–26] $\epsilon_\sigma/\epsilon_z \lesssim 1.5$, leading to the above estimate. In order to fulfill condition (16), an unphysically large value of $\epsilon_\sigma/\epsilon_z$ is required.

These parameters together with the crystal field energies $\epsilon_{3\mathrm{d}} = 1.0$ eV[24], $\lambda \simeq 0.1$ eV, $t_0 \simeq 1.0$ eV, and $\delta \simeq 0.05$[27], give the following estimates for the magnetic coupling constants: $J \simeq 0.13$ eV, $D \simeq 1.1$ meV, $\Gamma \simeq 8.3$ μeV, $\Gamma_2 \simeq 0.43$ μeV, and $\Gamma_z \simeq -23$ μeV. These results imply that $\Omega = 0.10 < \frac{1}{2}$, in accordance with the above discussion. The values for t_0 reported in the literature[24] are in the range 1.0 eV to 1.6 eV. Here we have chosen t_0 such that the experimental value $J \approx 130$ meV[28] is reproduced. For the calculation of Γ_2 we have estimated the crystal-field splitting $\epsilon_x - \epsilon_z = 0.1$ eV.

To conclude, although the magnetic coupling constants themselves are strongly dependent on the specific values of all the microscopic cuprate parameters, it is only the $g_{nn'}$ [Eq. (33)] which enter condition (16). Due to the restricted range of the 2p energies of oxygen, their realistic values clearly fail to comply with this condition. These results therefore do not allow for a weak ferromagnetic moment in the LTT phase of the cuprates based on the mechanisms included in our calculations. In particular, these results refute the recent claim of Koshibae, Ohta, and Maekawa[9] (KOM) that the LTT phase of the cuprates exhibits weak ferromagnetism due to the effect of the ligand energy levels. KOM obtain an expression for M_F in the LTO and the LTT phases and derive a criterion equivalent to (15) for the possible existence of weak ferromagnetism in the ground state configuration of the LTT phase. They *assume* that the mechanisms included in their calculation can provide a weak ferromagnetic moment. Under this assumption they then extract the magnetic coupling parameters by fitting their results for the spin-wave gaps to the experimental values obtained for $La_{1.65}Nd_{0.35}CuO_4$ and argue that these coupling parameters are consistent with the condition for weak ferromagnetism. However, KOM do not analyze further their criterion in terms of the microscopic cuprate parameters. Moreover, the assumption of a *vanishing* ferromagnetic moment in the LTT phase leads to values for their coupling parameters which are equally consistent with the criterion (15) and the observed results for the spin-wave gaps. Based on the experimental values for the spin-wave gaps obtained by Keimer *et al.*[3] [*cf.* section III], KOM derive the magnetic coupling constants which lead to $\Omega \simeq 4$ in the LTT phase with ferromagnetic canting of the spins, whereas in the LTT phase with vanishing ferromagnetic moment their results correspond to $\Omega \simeq -3$.

On the other hand, our calculations show that even in the general scenario for the magnetic anisotropies, as obtained in (3), which generalizes KOM's result, weak ferromagnetism is excluded for the LTT phase. This is also apparent from their criterion, if evaluated in terms of the corresponding cuprate parameters. For a nonvanishing ferromagnetic moment KOM's scenario would necessarily require $\epsilon_\sigma/\epsilon_z > 6.5$, which is certainly outside the physical range of the cuprate parameters.

Our result (14) for the weak ferromagnetic moment suggests that in $La_{2-x}Nd_xCuO_4$ the value for $M_F(\alpha)$ decreases as the temperature and dopant dependent tilting axis of the octahedra rotates from $\alpha = \pi/4$ to 0 upon lowering the temperature, and should finally vanish in the pure LTT phase. For $x < 0.35$, however, α is observed[3] to remain finite and one never reaches the LTT phase. Keimer *et al.*[3] found that in $La_{1.65}Nd_{0.35}CuO_4$ $\alpha \gtrsim 0.1$ also at low temperatures, and Shamoto *et al.*[5] encounter an orthorhombic distortion for $T > 20$ K. Although the results of Crawford *et al.*[4] are consistent with the occurrence of the LTT phase at 10 K, a rapid increase of the spontaneous magnetization for low temperatures is found,[5] which is ascribed[11] to the finite magnetic interaction of the Cu and Nd ions. Hence, the observed apparent persistence of the weak ferromagnetic moment in the LTT phase may be due to a coupling between the Cu and Nd spins which is not considered in our theory.

III. THE SPIN-WAVE GAPS

The experimental manifestation of the magnetic anisotropies are the gaps in the spin-wave spectrum. In order to derive these, we start with the diagonalized Hamiltonian (8) of the elementary plaquette and use the Holstein-Primakoff representation of the spin operators

$$\begin{aligned} &M_1'^z = S - a^\dagger a,\ M_1'^+ = \sqrt{2S}a,\ M_1'^- = \sqrt{2S}a^\dagger, \\ &M_2'^z = -S + b^\dagger b,\ M_2'^+ = \sqrt{2S}b^\dagger,\ M_2'^- = \sqrt{2S}b. \end{aligned} \quad (17)$$

Here we have chosen the $\hat{z}$-axis of the spins along the direction $\pm\hat{e}_+$ of the local staggered magnetic moment on the two sublattices. In terms of the spin-wave operators, and in the harmonic approximation, the magnetic Hamiltonian takes the form

$$\begin{aligned} \mathcal{H}' = &-4\Lambda_+ S^2 + 4\Lambda_+ S(a^+a + b^+b) + 2S(\Lambda_- + \Lambda_z) \\ &\times (a^+b^+ + ab) + 2S(\Lambda_- - \Lambda_z)(a^+b + ab^+). \end{aligned} \quad (18)$$

Diagonalizing this expression one finds two gaps,

$$\omega_{\substack{\text{out}\\ \text{in}}} = 4S\sqrt{(\Lambda_+ \pm \Lambda_-)(\Lambda_+ \mp \Lambda_z)}, \quad (19)$$

where $\omega_{\rm out}$ is the out-of-plane gap and $\omega_{\rm in}$ is the in-plane one. Introducing here the magnetic coupling parameters from Eqs. (9) these become

$$\omega_{\rm out} = 4JS\Bigg[-\frac{2\Gamma_z}{J} + \frac{\Gamma-\Gamma_2}{2J(1-\Omega)} \times (1-2\Omega+\sqrt{1-4\Omega(1-\Omega)\cos^2 2\alpha)}\Bigg]^{1/2},$$

$$\omega_{\rm in} = 4JS\left[\frac{\Gamma-\Gamma_2}{J(1-\Omega)}\sqrt{1-4\Omega(1-\Omega)\cos^2 2\alpha}\right]^{1/2}. \quad (20)$$

For $\Gamma_z = 0$, the gaps are degenerate for $\Omega = 0$, and also for nonzero Ω in the LTT phase, where $\alpha = 0$. The degeneracy of the gaps is lifted by the nonvanishing out-of-plane anisotropy $\Gamma_z < 0$. We also note that the in-plane-gap $\omega_{\rm in}$ goes to zero as the distortion of the oxygen octahedra vanishes and rotational invariance in the plane is restored, while for $\delta \to 0$ the nonzero Γ_z generates an easy-plane anisotropy in the HTT phase.

Although so far we have considered only a single plane, the above results remain valid also for the entire magnetic unit cell. In alternating planes the axis of rotation of the octahedra is tilted such that the value of α in one plane is replaced by $\pi/2-\alpha$ in the neighboring plane. This yields equivalent results for the spin-wave gaps.

A numerical evaluation of (20), using the microscopic cuprate parameters given above, leads to the values $\omega_{\rm in} \simeq 2.1$ meV and $\omega_{\rm out} \simeq 5.3$ meV in the LTO phase, and $\omega_{\rm in} \simeq 1.9$ meV and $\omega_{\rm out} \simeq 5.2$ meV in the LTT phase. Due to the small Ω, the gaps show only a weak variation over the whole range of α, giving almost identical values for the LTO and LTT phases. These results are to be compared with the experimental values of Keimer *et al.*[3], who found $\omega_{\rm in} = 2.3\pm0.5$ meV and $\omega_{\rm out} = 5.0\pm0.8$ meV in the LTO phase, and $\omega_{\rm in} = 4.5\pm0.5$ meV and $\omega_{\rm out} = 6.0\pm0.8$ meV near the LTT phase. Although the in-plane-gap of the LTT phase is underestimated by our calculation, our results capture the essential qualitative relations among the experimental values and give reasonable estimates for the out-of-plane gaps and the in-plane gap of the LTO phase. However, the differences of the gaps for the LTT and LTO phase as obtained from (20) are too small to explain the observed ones.

IV. DERIVATION OF THE MAGNETIC HAMILTONIAN

As mentioned, our derivation of the magnetic Hamiltonian is based on the perturbation expansion of a Hubbard model around the half-filled ground state. The microscopic Hamiltonian includes hopping between all orbitals on the copper d-states and on the oxygen p-states, and all on–site Coulomb interactions. In addition, the Hamiltonian contains the spin-orbit interactions on the copper. Those on the oxygen are assumed to be much smaller and are therefore neglected. General expressions for the effective magnetic interactions between two neighboring copper ions have already been derived,[21] but only the pure tetragonal symmetry has been considered in detail in this earlier work. In order to keep this paper self-contained, we outline here the main steps of the calculation and extend the results of Ref. 21 for general symmetry.

A significant simplification in the perturbation expansion is achieved by first treating the spin-orbit interactions *exactly*, leaving the expansion in orders of the spin-orbit coupling, λ, to the final stage. This is accomplished by introducing the unitary transformation which diagonalizes the single-particle part of the copper Hamiltonian,

$$\mathcal{H}_{\rm Cu} = \sum_{i\alpha\sigma}\epsilon_\alpha d^\dagger_{i\alpha\sigma}d_{i\alpha\sigma} + \frac{\lambda}{2}\sum_{i\alpha\beta}\sum_{\sigma\sigma'}\mathbf{L}_{\alpha\beta}\cdot[\sigma]_{\sigma\sigma'}d^\dagger_{i\alpha\sigma}d_{i\beta\sigma'} + \frac{1}{2}\sum_{\alpha\beta\gamma\delta}\sum_{i\sigma\sigma'}U_{\alpha\beta\gamma\delta}d^\dagger_{i\alpha\sigma}d^\dagger_{i\beta\sigma'}d_{i\gamma\sigma'}d_{i\delta\sigma}\,. \quad (21)$$

Here $d^\dagger_{i\alpha\sigma}$ creates a hole in the crystal-field state α with spin σ and energy ϵ_α on the copper at site i. For tetragonal symmetry, the crystal-field energies of holes at the copper ion obey[29] $\epsilon_{x^2-y^2} < \epsilon_{3z^2-r^2} < \epsilon_{xy} < \epsilon_{xz} = \epsilon_{yz}$. Even in the orthorhombic phase the site symmetry of each copper ion can be taken to be tetragonal, since the crystal field is primarily generated by neighboring oxygen ions, which, to a good approximation, still form an octahedron, albeit a rotated one. For tetragonal symmetry we label the crystal-field states as $|\,0\rangle \sim x^2-y^2$, $|1\rangle \sim 3z^2-r^2$, $|\,z\rangle \sim xy$, $|\,x\rangle \sim yz$, and $|\,y\rangle \sim zx$, where the z-axis is perpendicular to the CuO_2 plane and $|\,0\rangle$ is the lowest energy single–particle state. The second term in (21) is the spin-orbit interaction, where $\mathbf{L}_{\alpha\beta}$ denotes the matrix elements of the orbital angular momentum between the crystal-field states α and β. The last term is the Coulomb interaction, with $U_{\alpha\beta\gamma\delta} = \langle\alpha\delta|\beta\gamma\rangle$ in the notation[31] of Table A26 of Ref. 30. The unitary transformation that diagonalizes the single-particle part of $\mathcal{H}_{Cu}$ [given by the first two terms of Eq. (21)] can be written as[20,21]

$$d_{i\alpha\sigma} = \sum_{a\sigma'} m_{\alpha a}[\sigma(\alpha)]_{\sigma\sigma'}c_{ia\sigma'}, \quad (22)$$

where $c_{ia\sigma'}$ destroys a hole in the exact eigenstate of the Hamiltonian which consists of the crystal field and spin–orbit interactions. These states have a site label i, a state label (for which we use roman letters), and a pseudo–spin index σ'. In Eq. (22) we define $\sigma(\alpha)$ for each crystal-field state $|\,\alpha\rangle$ as follows: $\sigma(\alpha) = \sigma_\alpha$ is the Pauli matrix for $\alpha = x, y, z$ and $\sigma(\alpha) = I$ is the 2×2 unit matrix, for $\alpha = 0, 1$. The 5×5 matrix $\mathbf{m}$ is the solution to

$$\epsilon_\alpha m_{\alpha b} + \sum_\beta \mathcal{L}_{\alpha\beta}m_{\beta b} = E_b m_{\alpha b} \quad (23)$$

with $\sum_\alpha m^*_{\alpha a}m_{\alpha b} = \delta_{ab}$, where δ is the Kronecker delta function. Here all nonzero $\mathcal{L}_{\alpha\beta}$ are given by $\mathcal{L}_{0z} =$

$-i\lambda$, $\mathcal{L}_{0x} = \mathcal{L}_{0y} = i\lambda/2$, $\mathcal{L}_{1x} = -\mathcal{L}_{1y} = i\sqrt{3}\lambda/2$, $\mathcal{L}_{zx} = \mathcal{L}_{zy} = \mathcal{L}_{xy} = \lambda/2$. When $\lambda \to 0$, each state $|\,a\rangle$ approaches one of the states $|\,\alpha\rangle$. Using this identification, the indices a also run over the values $0, 1, z, x$, and y. The total Hamiltonian of the system,

$$\mathcal{H} = \mathcal{H}_{\rm Cu} + \mathcal{H}_O + \mathcal{H}_{\rm hop}, \tag{24}$$

in which $\mathcal{H}_O$ describes the Hamiltonian of the oxygens and $\mathcal{H}_{\rm hop}$ is the kinetic energy (hopping between Cu and O ions), is now divided into an unperturbed part, $\mathcal{H}_0$, and a perturbation term $\mathcal{H}_1$. The part $\mathcal{H}_0$ contains the single-particle Hamiltonians on the coppers and on the oxygens, *and* the leading on–site Coulomb potentials,

$$\mathcal{H}_0 = \sum_{ia\sigma} E_a c^\dagger_{ia\sigma} c_{ia\sigma} + \frac{U_0}{2} \sum_{\substack{iab\\ \sigma\sigma'}} c^\dagger_{ia\sigma} c^\dagger_{ib\sigma'} c_{ib\sigma'} c_{ia\sigma}$$
$$+ \sum_{kn\sigma} \epsilon_n p^\dagger_{kn\sigma} p_{kn\sigma} + \frac{U_P}{2} \sum_{\substack{knn'\\ \sigma\sigma'}} p^\dagger_{kn\sigma} p^\dagger_{kn'\sigma'} p_{kn'\sigma'} p_{kn\sigma} \ . \tag{25}$$

Here $p^\dagger_{kn\sigma}$ creates a hole in one of the three p-orbitals (denoted by n) on the oxygen at site k. We choose $U_0 \equiv U_{\alpha\alpha\alpha\alpha} = A + 4B + 3C$ and $U_P \equiv U_{nnnn} = F_0 + 4F_2$ for the leading on–site Coulomb interactions. We use the parametrization of the Coulomb matrix elements[30] in terms of the Racah coefficients A, B, and C for the copper d-states, with $A \gg B$, and $A \gg C$, and F_0 and F_2 for the oxygen p-states, with $F_0 \gg F_2$. The perturbation Hamiltonian $\mathcal{H}_1$ includes the kinetic energy and the remaining Coulomb interactions. Because of the transformation (22), the hopping becomes spin-dependent. Thus we have

$$\mathcal{H}_1 = \mathcal{H}_{\rm hop} + \Delta\mathcal{H}_C, \tag{26}$$

in which

$$\mathcal{H}_{\rm hop} = \sum_{ia\sigma} \sum_{kn\sigma'} (\tilde{t}^{ik}_{an})_{\sigma'\sigma} c^\dagger_{ia\sigma'} p_{kn\sigma} + {\rm hc}, \tag{27}$$

with the 2×2 matrix

$$\tilde{t}^{ik}_{an} = \sum_\alpha t^{ik}_{\alpha n} m^*_{\alpha a} \sigma(\alpha) \ , \tag{28}$$

and $\Delta\mathcal{H}_C$ describes the perturbation parts of the on–site Coulomb potentials,

$$\Delta\mathcal{H}_C = \frac{1}{2} \sum_{\substack{ss's_1s_1'\\ iabcd}} \Delta\bar{U}_{ss's_1s_1'}(abcd) c^\dagger_{ias} c^\dagger_{ibs'} c_{ics_1} c_{ids_1'}$$
$$+ \frac{1}{2} \sum_{\substack{k\sigma\sigma'\\ n_1n_2n_3n_4}} \Delta U_{n_1n_2n_3n_4} p^\dagger_{kn_1\sigma} p^\dagger_{kn_2\sigma'} p_{kn_3\sigma'} p_{kn_4\sigma}, \tag{29}$$

with

$$\Delta\bar{U}_{ss's_1s_1'}(abcd) = \sum_{\alpha\beta\gamma\delta} \Delta U_{\alpha\beta\gamma\delta}$$
$$\times m^*_{\alpha a} m^*_{\beta b} m_{\gamma c} m_{\delta d} [\sigma(\alpha)\sigma(\delta)]_{ss_1'} [\sigma(\beta)\sigma(\gamma)]_{s's_1}. \tag{30}$$

Here we have defined $\Delta U_{\alpha\beta\beta\alpha} = U_{\alpha\beta\beta\alpha} - U_0$ and $\Delta U_{nn'n'n} = U_{nn'n'n} - U_P$. For $\alpha \neq \delta$ or $\beta \neq \gamma$, and $n_1 \neq n_4$ or $n_2 \neq n_3$, we take $\Delta U_{\alpha\beta\gamma\delta} = U_{\alpha\beta\gamma\delta}$ and $\Delta U_{n_1n_2n_3n_4} = U_{n_1n_2n_3n_4}$, respectively. Note that $\mathbf{\Delta U}$ involves only the small Racah coefficients, B, C, and F_2.

The effective magnetic interaction $\mathcal{H}(i,j)$ between magnetic ions i and j is found by perturbation expansion with respect to $\mathcal{H}_1$. The lowest-order contributions to the energy are of order $\tilde{t}^4$ and read

$$\mathcal{H}^{(1)}(i,j) = \sum_{nn'} g_{nn'} {\rm Tr}\Big\{\sigma \cdot \mathbf{S}_i \tilde{t}^{ik}_{0n} \tilde{t}^{kj}_{n0} \sigma \cdot \mathbf{S}_j \tilde{t}^{jk}_{0n'} \tilde{t}^{ki}_{n'0}\Big\} \ , \tag{31}$$

in which

$$\mathbf{S}_i = \frac{1}{2} \sum_{\sigma\sigma'} c^\dagger_{i0\sigma} (\sigma)_{\sigma\sigma'} c_{i0\sigma'}, \tag{32}$$

is the spin on the copper at site i in the orbital state $|\,0\rangle$, $\tilde{t}^{ik}_{0n}$ is the 2×2 matrix given by Eq. (28) and

$$g_{nn'} = \frac{2}{U_0} \frac{1}{\epsilon_n \epsilon_{n'}}$$
$$+ \frac{1}{U_P + U_{nn'n'n} + \epsilon_n + \epsilon_{n'}} \Big(\frac{1}{\epsilon_n} + \frac{1}{\epsilon_{n'}}\Big)^2. \tag{33}$$

In deriving expression (31) we have assumed that the single-particle energy $E_{a=0}$ on the copper is equal to zero.

Next we consider the contributions to the magnetic energy which are of order $\tilde{t}^4$ and first order in $\Delta\mathcal{H}_C$. The contribution of the processes in which the two holes are on the same copper in intermediate states is indicated by a subscript "a", and that in which the two holes are on the oxygen is denoted by "b". One finds[20,21]

$$\mathcal{H}^{(2)}_a(i,j) =$$
$$\sum_{a,b\neq 0} \Bigg[Q_{ab} {\rm Tr}\Big\{\sigma \cdot \mathbf{S}_i \sum_n \frac{\tilde{t}^{ik}_{0n} \tilde{t}^{kj}_{nb}}{\epsilon_n} \sigma \cdot \mathbf{S}_j \sum_{n'} \frac{\tilde{t}^{jk}_{an'} \tilde{t}^{ki}_{n'0}}{\epsilon_{n'}}\Big\}$$
$$+ \sum_\mu K^\mu_{ab} S_{j\mu} {\rm Tr}\Big\{\sigma \cdot \mathbf{S}_i \sum_n \frac{\tilde{t}^{ik}_{0n} \tilde{t}^{kj}_{nb}}{\epsilon_n} \sigma_\mu \sum_{n'} \frac{\tilde{t}^{jk}_{an'} \tilde{t}^{ki}_{n'0}}{\epsilon_{n'}}\Big\}$$
$$+ (i \leftrightarrow j)\Bigg], \ \mu = x, y, z, \tag{34}$$

with

$$Q_{ab} = \sum_{\alpha\beta\gamma\delta} \frac{U^{(2)}_{\alpha\beta\gamma\delta} - U^{(1)}_{\alpha\beta\gamma\delta}}{(U_0 + E_a)(U_0 + E_b)} m^*_{\alpha b} m^*_{\beta 0} m_{\gamma a} m_{\delta 0}, \tag{35a}$$

and

$$K^\mu_{ab} = \sum_{\alpha\beta\gamma\delta} \frac{U^{(2)}_{\alpha\beta\gamma\delta}}{(U_0 + E_a)(U_0 + E_b)}$$
$$\times (m^*_{\alpha b} m^*_{\beta 0} - m^*_{\beta b} m^*_{\alpha 0})(m_{\delta a} m_{\gamma 0} - m_{\delta 0} m_{\gamma a}). \tag{35b}$$

The Coulomb matrix elements $U_{\alpha\beta\gamma\delta}$ vanish unless the values of $\alpha,\beta,\gamma,\delta$ are such that the products $\sigma(\alpha)\sigma(\delta)$ and $\sigma(\beta)\sigma(\gamma)$ are proportional to each other. This is due to symmetry and can easily be verified by inspection of the explicit expressions for the general nonzero Coulomb terms.[30] Here we define $U^{(1)}_{\alpha\beta\gamma\delta}$ and $U^{(2)}_{\alpha\beta\gamma\delta}$ such that for the elements denoted $U^{(1)}_{\alpha\beta\gamma\delta}$ the products $\sigma(\alpha)\sigma(\delta)$ and $\sigma(\beta)\sigma(\gamma)$ are both proportional to the unit matrix. For the matrix elements denoted by $U^{(2)}_{\alpha\beta\gamma\delta}$, both products are proportional to σ_μ, with $\mu = x, y$, or z.

In a similar way, we find

$$\begin{aligned}\mathcal{H}^{(2)}_b(i,j) &= \sum_{n\neq n'}\Big(\frac{1}{\epsilon_n}+\frac{1}{\epsilon_{n'}}\Big)^2\frac{\Delta U_{nn'nn'}}{(U_P+\epsilon_n+\epsilon_{n'})^2}\\ &\times\Bigg[\mathrm{Tr}\Big\{\sigma\cdot\mathbf{S}_i\tilde{t}^{ik}_{0n}\tilde{t}^{ki}_{n'0}\Big\}\mathrm{Tr}\Big\{\sigma\cdot\mathbf{S}_j\tilde{t}^{jk}_{0n'}\tilde{t}^{kj}_{n0}\Big\}\\ &-\mathrm{Tr}\Big\{\sigma\cdot\mathbf{S}_i\tilde{t}^{ik}_{0n}\tilde{t}^{kj}_{n'0}\sigma\cdot\mathbf{S}_j\tilde{t}^{jk}_{0n'}\tilde{t}^{ki}_{n0}\Big\}\Bigg]\\ &+\sum_{n\neq n'}\frac{4}{\epsilon_n\epsilon_{n'}}\frac{\Delta U_{nnn'n'}}{(U_P+2\epsilon_n)(U_P+2\epsilon_{n'})}\\ &\times\Bigg[\mathrm{Tr}\Big\{\sigma\cdot\mathbf{S}_i\tilde{t}^{ik}_{0n}\tilde{t}^{ki}_{n'0}\Big\}\mathrm{Tr}\Big\{\sigma\cdot\mathbf{S}_j\tilde{t}^{jk}_{0n}\tilde{t}^{kj}_{n'0}\Big\}\\ &-\mathrm{Tr}\Big\{\sigma\cdot\mathbf{S}_i\tilde{t}^{ik}_{0n}\tilde{t}^{kj}_{n'0}\sigma\cdot\mathbf{S}_j\tilde{t}^{jk}_{0n}\tilde{t}^{ki}_{n'0}\Big\}\Bigg]. \qquad (36)\end{aligned}$$

Here and in (33) we have included all non zero matrix elements $\Delta U_{nn_1n_2n_3}$.[30]

To the order we work, the total magnetic interaction between a pair of copper ions is given by the sum of the three contributions,

$$\mathcal{H}(i,j) = \mathcal{H}^{(1)}(i,j) + \mathcal{H}^{(2)}_a(i,j) + \mathcal{H}^{(2)}_b(i,j). \qquad (37)$$

To obtain explicit expressions for the magnetic couplings [*cf.* Eq. (1)] requires the detailed forms of the effective hopping between the copper ions, $\tilde{t}^{ik}_{an}\tilde{t}^{kj}_{n'b}$. These are evaluated in the next section, where we derive the effective magnetic interactions between the coppers.

V. DERIVATION OF THE MAGNETIC COUPLINGS

To obtain the magnetic energy (1), one has to sum $\mathcal{H}(i,j)$ [Eq. (37)] over the plaquette, see Fig. 1. This necessitates the computation of the effective hopping between the copper ions, given by [*cf.* Eq. (28)]

$$\tilde{t}^{ik}_{an}\tilde{t}^{kj}_{n'b} = \sum_{\alpha\beta} t^{ik}_{\alpha n}t^{kj}_{n'\beta}m^*_{\alpha a}m_{\beta b}\sigma(\alpha)\sigma(\beta), \qquad (38)$$

in which $\mathbf{m}$ is given by (23). [Eq. (36) requires also the cases $i = j$.] Here the site index k refers to the oxygen ion in between the two coppers. Since in the following we distinguish between Cu-Cu bonds along $\hat{x}$ and along $\hat{y}$, the oxygen site index will be omitted for convenience. In tetragonal symmetry the only nonzero hopping matrix elements $t_{\alpha n}$ are t_{0p_x}, t_{1p_x}, t_{yp_z}, and t_{zp_y} for a bond directed along $\hat{x}$ in the CuO_2 plane, and analogously t_{0p_y}, t_{1p_y}, t_{xp_z}, and t_{zp_x} for a bond along $\hat{y}$. These can be expressed in terms of $(pd\sigma)$ and $(pd\pi)\approx -\frac{1}{2}(pd\sigma)$,[32]

$$\begin{aligned}t_0 &\equiv -t_{0p_x} = t_{0p_y} = -\frac{\sqrt{3}}{2}(pd\sigma),\\ t_1 &\equiv t_{1p_x} = t_{1p_y} = -\frac{1}{2}(pd\sigma),\\ t_2 &\equiv t_{yp_z} = t_{zp_y} = t_{xp_z} = t_{zp_x} = (pd\pi). \qquad (39)\end{aligned}$$

In the orthorhombic phase, in which the oxygens rotate around the $\hat{n}$-axis by a small angle δ, the hopping matrix elements are those between the rotated orbitals. A reasonable approximation is to take account of the orthorhombic distortion by considering the crystal-field states of the oxygen octahedron assuming that it rotates rigidly. Then, to the extent that the crystal field is determined by the oxygen neighbors alone, it will be tetragonal in the rotated coordinate frame fixed by the shell of oxygen neighbors. The hopping elements in the rotated frame computed in this way are listed in Table I (for the Cu-Cu bond along $\hat{x}$), and in Table II (for a bond in the $\hat{y}$-direction). These, together with the matrix elements of $\mathbf{m}$ listed in Table III, are used in Eq. (38) to find the effective hopping between the copper ions.

Some comments concerning the following computations should be made. Our goal is to calculate the magnetic energy up to order $\lambda^2\delta^2$. This requires the evaluation of the Dzyaloshinskii-Moriya vector $\mathbf{D}$ up to order $\lambda\delta$, since its contribution to the magnetic energy is of order D^2 (see Sec. II). The isotropic coupling J will be found to the lowest possible order, and contributions to it which involve powers of λ, δ, or Coulomb corrections $\mathbf{\Delta U}$ will be disregarded. The reason for this is two-fold. First,[20] although the use of perturbation theory is justified for the calculation of the anisotropic magnetic interactions, it is not reliable for the computation of the isotropic terms, because the energies of the excited states are not very large compared to $\mathbf{t}$. This effect is reduced in the anisotropic couplings since they are generated by terms proportional to λ or to δ.[20] Second, there are contributions to the isotropic energy coming from processes not included in the discussion of a single bond.[33]

We first find the magnetic energy resulting from $\mathcal{H}^{(1)}(i,j)$, Eqs. (31) and (33). The relevant effective hopping elements are

$$\begin{aligned}\tilde{t}^1_{0p_x}\tilde{t}^2_{p_x0} &= -t_0^2 + it_0t_2\frac{\lambda}{\epsilon_x}\delta\sin\alpha\sigma_y,\\ \tilde{t}^1_{0p_z}\tilde{t}^2_{p_z0} &= it_0t_2\frac{\lambda}{\epsilon_x}\delta\sin\alpha\sigma_y, \qquad (40)\end{aligned}$$

for a bond along $\hat{x}$, and

$$\tilde{t}^1_{0p_y}\tilde{t}^2_{p_y0} = -t_0^2 + it_0t_2\frac{\lambda}{\epsilon_x}\delta\cos\alpha\sigma_x,$$
$$\tilde{t}^1_{0p_z}\tilde{t}^2_{p_z0} = it_0t_2\frac{\lambda}{\epsilon_x}\delta\cos\alpha\sigma_x, \tag{41}$$

for a bond along $\hat{y}$. Inserting these expressions into (31), summing over the four bonds of the plaquette and dividing by the number of bonds yields

$$J = 2g_{p_\sigma p_\sigma}t_0^4,\quad D = 2t_0^3t_2\frac{\lambda\delta}{\epsilon_x}\Big(g_{p_\sigma p_\sigma}+g_{p_\sigma p_z}\Big),$$
$$\Gamma = 2t_2^2t_0^2\Big(g_{p_\sigma p_\sigma}+g_{p_z p_z}+2g_{p_\sigma p_z}\Big)\Big(\frac{\lambda\delta}{\epsilon_x}\Big)^2,$$
$$\Gamma_z = 0,\ \Gamma_2 = 0. \tag{42}$$

Here we have introduced the notations $p_\sigma = p_x$ or p_y for a bond along $\hat{x}$ or $\hat{y}$, respectively. (Similarly, we will use $p_\pi = p_y$ or p_x.)

The contributions coming from $\mathcal{H}^{(2)}_{a,b}(i,j)$ are necessarily smaller than those arising from $\mathcal{H}^{(1)}(i,j)$, as they involve the smaller Racah coefficients B and C, and F_2, divided by the leading Coulomb energies A and F_0, respectively.[23,25] In addition, they only lead to anisotropies which are also of the form of Eqs. (2) and (3). In view of this, one may ignore corrections to the couplings J, D, and Γ, introduced by the processes $\mathcal{H}^{(2)}_{a,b}$, and concentrate on the anisotropies indicated by Γ_z and Γ_2 [see Eq. (3)], which are not contained in $\mathcal{H}^{(1)}$. A detailed calculation of $\mathcal{H}^{(2)}_b$, in conjunction with Eq. (38) has shown that these processes give rise only to corrections to J, D, and Γ, and do not generate anisotropies of the form of Γ_z or Γ_2. This is not the case for the contributions coming from $\mathcal{H}^{(2)}_a$. The reason is related to the neglect of spin-orbit interactions on the oxygens. We therefore omit further discussion of the contributions generated by the processes in which the two holes are on the oxygen in intermediate states.

An analogous argument applies to the magnetic anisotropies due to the direct exchange interaction, involving *nonlocal* Coulomb matrix elements. These only generate anisotropies which are of the form of Eqs. (2) and (3) and are generally much smaller than the leading contributions from the kinetic superexchange.[22] Therefore, as is shown in detail elsewhere,[22] for the discussion of the magnetic order in the ground state the contributions from the direct exchange mechanism can be neglected.

Next we investigate the contributions of the processes contained in $\mathcal{H}^{(2)}_a$, in which the two holes occupy the same copper ion in intermediate states. We note that the summation indices a and b of Eq (34) can take the values $|a\rangle,|b\rangle = |1\rangle$ or $|a\rangle,|b\rangle = |x\rangle,|y\rangle$, or $|z\rangle$. We therefore need to evaluate the effective Cu-Cu hopping for these values. Up to the required accuracy we find

$$t^{12}_{01} \equiv \sum_n \frac{\tilde{t}^1_{0n}\tilde{t}^2_{n1}}{\epsilon_n} = \frac{t_0t_1}{\epsilon_{p_\sigma}} + i\chi\sin\alpha\sigma_y,$$

$$t^{21}_{01} \equiv \sum_n \frac{\tilde{t}^2_{0n}\tilde{t}^1_{n1}}{\epsilon_n} = \frac{t_0t_1}{\epsilon_{p_\sigma}} - i\chi\sin\alpha\sigma_y,$$
$$\chi = \frac{\lambda\delta t_2}{2}\Big(\frac{1}{\epsilon_{p_\sigma}}+\frac{1}{\epsilon_{p_z}}\Big)\Big(\frac{\sqrt{3}t_0}{\epsilon_1-\epsilon_x}-\frac{t_1}{\epsilon_x}\Big) \tag{43}$$

for a bond along $\hat{x}$. The corresponding expressions for a bond along $\hat{y}$ are obtained from (43) by the replacements $x \leftrightarrow y$, $t_0 \leftrightarrow -t_0$, and $\sin\alpha \leftrightarrow -\cos\alpha$.

Similarly, for $\mu = x, y$ or z one obtains

$$t^{12}_{0\mu} \equiv \sum_n \frac{\tilde{t}^1_{0n}\tilde{t}^2_{n\mu}}{\epsilon_n} = b^\mu + i\sigma\cdot\mathbf{v}^\mu,$$
$$t^{21}_{0\mu} = b^\mu - i\sigma\cdot\mathbf{v}^\mu, \tag{44}$$

with

$$b^\mu = \frac{1}{\epsilon_{p_\sigma}}(-t_0^2m_{0\mu}+t_0t_1m_{1\mu}) - \frac{i\lambda}{\epsilon_{p_\pi}\epsilon_z}t_2^2m_{z\mu} + \frac{i\lambda}{2\epsilon_{p_z}\epsilon_x}t_2^2m_{y\mu}, \tag{45}$$

for a bond along $\hat{x}$. Again, to find b^μ for a bond in the $\hat{y}$-direction, the aforementioned replacements should be made. The expressions for $\mathbf{v}^\mu$ are given by

$$\mathbf{v}^\mu = \Big[-i\Big(\frac{1}{\epsilon_{p_\pi}}+\frac{1}{\epsilon_{p_z}}\Big)t_2^2\Big(\frac{\lambda}{\epsilon_z}m_{y\mu}-\frac{\lambda}{2\epsilon_x}m_{z\mu}\Big)\delta\cos\alpha,\ -i\Big(\frac{1}{\epsilon_{p_\sigma}}+\frac{1}{\epsilon_{p_z}}\Big)t_0t_2m_{y\mu}\delta\sin\alpha,\ 0\Big], \tag{46a}$$

and

$$\mathbf{v}^\mu = \Big[-i\Big(\frac{1}{\epsilon_{p_\sigma}}+\frac{1}{\epsilon_{p_z}}\Big)t_0t_2m_{x\mu}\delta\cos\alpha,\ -i\Big(\frac{1}{\epsilon_{p_\pi}}+\frac{1}{\epsilon_{p_z}}\Big)\times t_2^2\Big(\frac{\lambda}{\epsilon_z}m_{x\mu}-\frac{\lambda}{2\epsilon_x}m_{z\mu}\Big)\delta\sin\alpha,\ 0\Big], \tag{46b}$$

for a bond along $\hat{x}$ and along $\hat{y}$, respectively. Here we have not yet introduced the explicit expressions for the matrix elements of $\mathbf{m}$ involving the index μ (Table III).

We next insert Eqs. (43-46) into (34). Omitting higher-order corrections to the magnetic couplings given in (42), we find that the nonzero contributions to Γ_2 are

$$\Gamma_2 = -\frac{2\delta^2\lambda^2}{\epsilon_x(\epsilon_z-\epsilon_x)}\Big(\frac{1}{\epsilon_{p_\sigma}}+\frac{1}{\epsilon_{p_z}}\Big)\Big(\frac{1}{\epsilon_{p_\pi}}+\frac{1}{\epsilon_{p_z}}\Big)\frac{t_0t_2^3U^{(2)}_{0z0z}}{(U_0+\epsilon_z)^2}. \tag{47}$$

To the leading order, for Γ_z it is sufficient to obtain the contributions in the pure tetragonal phase.[21] We derive

$$\Gamma_z = -8\lambda^2\frac{U^{(2)}_{0z0z}}{(U_0+\epsilon_z)^2}\Big[\frac{1}{\epsilon_z}\Big(\frac{t_0^2}{\epsilon_{p_\sigma}}-\frac{t_2^2}{\epsilon_{p_\pi}}\Big)\Big]^2 - 8\lambda^2\frac{U^{(2)}_{1z1z}}{(U_0+\epsilon_1)^2}$$

$$\times \Big(\frac{t_0t_1}{\epsilon_z\epsilon_{p_\sigma}}\Big)^2 + \lambda^2\frac{U^{(2)}_{0x0x}}{(U_0+\epsilon_x)^2}\Big[\Big(\frac{\sqrt{3}}{U_0+\epsilon_1}\frac{t_0t_1}{\epsilon_{p_\sigma}} + \frac{t_0^2}{\epsilon_x\epsilon_{p_\sigma}}\Big)^2 + \Big(\frac{\sqrt{3}}{U_0+\epsilon_1}\frac{t_0t_1}{\epsilon_{p_\sigma}} - \frac{1}{\epsilon_x}\big(\frac{t_0^2}{\epsilon_{p_\sigma}} - \frac{t_2^2}{\epsilon_{p_z}}\big)\Big)^2\Big] + 2\lambda^2\frac{U^{(2)}_{1x1x}}{(U_0+\epsilon_1)^2}\Big(\frac{t_0t_1}{\epsilon_x\epsilon_{p_\sigma}}\Big)^2 - 2\lambda^2\frac{U^{(2)}_{0x1x}}{(U_0+\epsilon_1)(U_0+\epsilon_x)} \times \frac{t_0t_1}{\epsilon_x\epsilon_{p_\sigma}}\Big[\frac{t_2^2}{\epsilon_x\epsilon_{p_z}} + \frac{2\sqrt{3}}{U_0+\epsilon_1}\frac{t_0t_1}{\epsilon_{p_\sigma}}\Big]. \quad (48)$$

Here we have used the relations[30] $U^{(2)}_{0x0x} = U^{(2)}_{0y0y}$, $U^{(2)}_{1x1x} = U^{(2)}_{1y1y}$, and $U^{(2)}_{0x1x} = -U^{(2)}_{0y1y}$.

VI. SUMMARY

To summarize, we have derived the anisotropic magnetic Hamiltonian of the copper-oxide plane based on an extended perturbation theory, including spin-orbit coupling on the transition metal, hopping between excited states of neighboring copper and oxygen ions, and the effect of general local Coulomb interactions. We have considered the explicit dependence on the orbitals of the transition metal and ligand ions, and the different low-temperature phases of the La_2CuO_4-type materials, allowing for a general rotation axis of the CuO_6 octahedra.

We have found the magnetic order in the classical ground state of the anisotropic spin interaction and have derived a general expression for the planar weak ferromagnetic moment, depending on the orientation of the tilting axis of the octahedra. The general condition $\Omega > 1/2$ for the occurrence of weak ferromagnetism in the LTT phase of the cuprates has been obtained and analyzed for realistic cuprate parameters. Our calculations yield $\Omega \simeq 0.10$ and therefore do *not* predict a weak ferromagnetic moment in this phase. As the tilting axis of the oxygen octahedra rotates from $\pi/4$ in the LTO phase to zero in the LTT phase, the planar spontaneous magnetization decreases continuously, vanishing in the LTT limit.

However, our theory does not consider the possible coupling of the Cu spins to the magnetic moments of the doped Nd ions, which may be the source of an out-of-plane canting of the Cu spins at low temperatures. This is also suggested by the measured correlation between the size of the weak ferromagnetic moment and the amount of Nd doping.[34]

Our results for the spin-wave gaps give good estimates for the experimental values within the error bars of the measurements, but cannot explain the observed splitting of the gaps between the LTO and LTT phase. The observed value of the in-plane gap in the LTT phase is underestimated by our calculation by a factor of two, which may also be due to the neglect of the coupling to the Nd spins.

Finally, the perturbation analysis carried out in the present paper does not include the effect of nonlocal Coulomb interactions. Their contributions to the magnetic Hamiltonian, however, may be omitted as small, since they do not generate a qualitatively different anisotropic spin interaction.[22]

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TABLE I. Hopping matrix elements for a bond along $\hat{x}$. The first row indicates the oxygen orbitals; in the left column appear the copper d-orbitals. The upper signs pertain for the copper ion 1, the lower for the copper ion 2, see Fig. 1)

	p_x	p_y	p_z
0	$\mp t_0$	0	$-t_0\delta\sin\alpha$
1	$\pm t_1$	0	$t_1\delta\sin\alpha$
z	0	$\pm t_2$	$-t_2\delta\cos\alpha$
x	0	0	0
y	$-t_2\delta\sin\alpha$	$t_2\delta\cos\alpha$	$\pm t_2$

TABLE II. Hopping matrix elements for a bond along $\hat{y}$. (The notations are the same as in Table 1.)

	p_x	p_y	p_z
0	0	$\pm t_0$	$-t_0\delta\cos\alpha$
1	0	$\pm t_1$	$-t_1\delta\cos\alpha$
z	$\pm t_2$	0	$t_2\delta\sin\alpha$
x	$-t_2\delta\sin\alpha$	$t_2\delta\cos\alpha$	$\pm t_2$
y	0	0	0

TABLE III. The matrix $\mathbf{m}$, to first order in the spin-orbit coupling λ. Note that $\epsilon_x = \epsilon_y$. The entries correspond to $m_{\alpha a}$.

1	0	$-i\frac{\lambda}{\epsilon_z}$	$i\frac{\lambda}{\sqrt{2}\epsilon_x}$	0
0	1	0	0	$-i\sqrt{\frac{3}{2}}\frac{\lambda}{\epsilon_1-\epsilon_x}$
$-i\frac{\lambda}{\epsilon_z}$	0	1	$\frac{\lambda}{\sqrt{2}(\epsilon_x-\epsilon_z)}$	0
$i\frac{\lambda}{2\epsilon_x}$	$-i\frac{\sqrt{3}\lambda}{2(\epsilon_1-\epsilon_x)}$	$\frac{\lambda}{2(\epsilon_z-\epsilon_x)}$	$\sqrt{\frac{1}{2}}$	$\sqrt{\frac{1}{2}}$
$i\frac{\lambda}{2\epsilon_x}$	$i\frac{\sqrt{3}\lambda}{2(\epsilon_1-\epsilon_x)}$	$\frac{\lambda}{2(\epsilon_z-\epsilon_x)}$	$\sqrt{\frac{1}{2}}$	$-\sqrt{\frac{1}{2}}$

FIGURE CAPTIONS

Figure 1: The CuO_2 plane of the intermediate (LTO2) phase of $La_{2-x}Nd_xCuO_4$. The squares represent Cu ions, the circles are oxygen ions. The oxygen octahedra rotate around the $\hat{n}$ axis.

Figure 2: The ferromagnetic moment $M_F(\alpha)/(SD/2J)$ versus α for $\Omega = 0.10$ (solid line), $\Omega = 0.51$ (dashed line), and $\Omega = 0.49$ (dotted line).