Nonlocal Coulomb interactions and the magnetic anisotropies in the low-temperature phases of the cuprates

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We have extended and generalized earlier studies of the magnetic anisotropies of the Cu spins in the copper-oxide planes generated by the spin-orbit coupling on the coppers and by the *nonlocal* Coulomb interactions between neighboring ions. Our derivation of the anisotropic magnetic Hamiltonian includes the contributions from general matrix elements of the Coulomb interaction both between the copper ions of a single bond and between the adjacent copper and oxygen sites. The results apply for a general rotation axis of the oxygen octahedra, with the assumption of tetragonal site symmetry of the copper. This mechanism leads to a form of the anisotropic spin interaction between the Cu ions which is identical to the one generated by kinetic superexchange in the presence of purely *local* Coulomb interactions. Together with the numerical estimates for the resulting spin couplings, this indicates that the Coulomb direct exchange leads to significant contributions to the isotropic spin interaction and the out-of-plane anisotropy, but does not affect qualitatively the magnetic order in the ground state.

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I. INTRODUCTION

In the orthorhombic phase of La_2CuO_4-type compounds, the axis of the CuO_6 octahedra tilts slightly at low temperatures.[1,2] The structural distortion together with the spin-orbit interaction on the transition metal ions leads to various magnetic anisotropies. These comprise the antisymmetric Dzyaloshinskii-Moriya interaction[3] as well as symmetric anisotropies which are equally important for the determination of the magnetic ground state.[4]

Generally, the study of these magnetic anisotropies[5–11] is based on Moriya's extension[12] of Anderson's theory[13] of kinetic superexchange. The importance of the on-site Coulomb exchange interactions within the theory of kinetic superexchange has been noted recently.[14] These lead to an easy-plane anisotropy also in the absence of structural distortions, as is observed in many purely tetragonal systems. Moreover, in the distorted low-temperature phases of the La_2CuO_4-based cuprates the Coulomb exchange terms and additional general local Coulomb matrix elements involving more than two orbitals[15] also allow for nondiagonal contributions to the symmetric anisotropy tensor.[16]

Since the magnetic ground state depends in a subtle way on the detailed form of the anisotropic spin interaction, it is crucial to include all possible types of anisotropies in the ground state analysis of the magnetic Hamiltonian. A detailed understanding of the role of the on-site Coulomb interactions with respect to the resulting magnetic couplings in the low-symmetry phases of the cuprates has already been achieved.[15,16] However, although the importance of the Coulomb direct exchange interactions between neighboring ions for the magnetic anisotropies is well known since the work of Moriya,[12] nonlocal interaction effects in the copper-oxide planes have only been considered for the undistorted tetragonal case in previous studies. These include the calculation of the (ferromagnetic) isotropic Heisenberg term due to copper-oxygen exchange,[17–19] and of the easy-plane anisotropy due to spin-orbit interactions and the direct exchange between coppers.[10,20] Besides the neglect of the lattice distortion at low temperatures, these previous results were derived including only the largest Coulomb terms, while more general matrix elements of a comparable order of magnitude were disregarded. These, however, also contribute to additional anisotropies in the distorted phases. For the analysis of the magnetic ground state it is therefore essential to clarify the effect of general nonlocal Coulomb interactions on the various magnetic anisotropies.

In the present paper we generalize and extend the earlier calculations[10,17,20] in several directions. We analyze in detail the contributions to the anisotropic magnetic Hamiltonian which originate from the general Coulomb direct exchange interactions, the spin-orbit coupling on the coppers, and the lattice distortion in the low-temperature phases. We consider *general* nonlocal Coulomb matrix elements between the two copper ions of a single bond as well as those between the neighboring copper and oxygen sites. The axis of rotation of the oxygen octahedra is taken to have a general orientation in the copper-oxide plane. This is of particular importance for the doped $La_{2-x}Nd_xCuO_4$ system, in which the oxygen octahedra tilt about an axis whose direction depends on the temperature and on the dopant concentration.[2]

The results of this paper complement the derivations of the anisotropic magnetic interaction in the cuprates within the theory of kinetic superexchange with general *local* Coulomb interactions.[16] As the most important result, it is found that the direct exchange mechanism generates anisotropies which are not qualitatively different from those due to general *local* Coulomb matrix elements. The numerical estimates for the resulting spin couplings show that the nonlocal Coulomb interactions do not affect qualitatively the magnetic order in the ground state, but contribute significantly to the isotropic spin coupling constant and to the out-of-plane anisotropy. The improved result for the out-of-plane anisotropy may also yield a better estimate for the spin-wave gap.

The effective magnetic Hamiltonian for the Cu spins is derived by a perturbative treatment of the Hubbard Hamiltonian of a single Cu-O-Cu bond around the half-filled ground state, in which one hole resides in the $3d_{x^2-y^2}$ orbital on each Cu ion. This is facilitated by first diagonalizing the single-particle part of the copper Hamiltonian, including the crystal-field energies and the spin-orbit coupling.[15] The hopping between copper and oxygen states and the Coulomb interactions are treated perturbatively.

The resulting magnetic interactions between two neighboring copper ions are then added together on the four bonds of the elementary plaquette of the CuO_2 plane [*cf.* Fig. 1 of Ref. 16]. With the sublattice magnetizations $\mathbf{M}_1$ and $\mathbf{M}_2$, the magnetic Hamiltonian of the plaquette related to the Coulomb direct exchange interaction then generally reads

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

The oxygen octahedra surrounding each copper ion in the La_2CuO_4-type compounds tilt alternately by a small angle δ about a general axis $\hat{n} = \hat{x}\cos\alpha + \hat{y}\sin\alpha$ in the copper-oxide plane, with its orientation depending on temperature and doping [*cf.* Fig. 1 of Ref. 16]. With the spin-orbit coupling factor λ, we find that to order $\lambda^2\delta^2$ in the magnetic energy (i.e., to order $\lambda\delta$ in $\mathbf{D}$ and order $\lambda^2\delta^2$ in $\mathbf{\Gamma}$) the Dzyaloshinskii-Moriya vector $\mathbf{D} = D\hat{n}$ is directed along the rotation axis of the oxygen octahedra, $\hat{n}$, and the symmetric tensor $\mathbf{\Gamma}$ is given by

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

This has the same form as in the case of kinetic superexchange with purely local Coulomb interactions.[16] Denoting the hopping between the copper $3d_{x^2-y^2}$ and oxygen $2p_\sigma$ states by t_0, and the matrix elements of the Coulomb direct exchange interactions between the coppers and between copper and oxygen by V and K, respectively, the leading contributions to the coupling constants of this effective planar magnetic Hamiltonian are of the following form:

$$\begin{aligned} &J \sim V + t_0^2 K,\ \Gamma_z \sim \lambda^2(V + t_0^2 K), \\ &D \sim t_0^2\lambda\delta K, \quad \text{and} \quad \Gamma, \Gamma_2 \sim t_0^2\lambda^2\delta^2 K. \end{aligned} \quad (3)$$

From these results it is apparent that the direct exchange interaction between the copper ions only enters into the coupling of the dominant isotropic Heisenberg term and into the out-of-plane anisotropy Γ_z. All other coupling constants are determined solely by the direct exchange between copper and oxygen sites. Note that direct exchange contributions only to J and Γ_z have been obtained in previous work.[10,17,20]

The detailed derivation of the effective magnetic Hamiltonian for the copper-oxide planes in order $\mathcal{O}(\lambda^2\delta^2)$ is described in section II. The explicit results and numerical estimates for the coupling constants, retaining the general orbital dependence of all involved Coulomb matrix elements, are presented in section III. Finally, section IV contains a discussion of our results.

II. THE MAGNETIC HAMILTONIAN DUE TO DIRECT COULOMB EXCHANGE

As has been noted previously,[15,16] a considerable simplification of the perturbation expansion is achieved by first treating the spin-orbit interactions exactly, introducing the unitary transformation which diagonalizes the single-particle part of the copper Hamiltonian,

$$\mathcal{H}_{\rm Cu} = \sum_{i\alpha\sigma} \epsilon_\alpha d^\dagger_{i\alpha\sigma} d_{i\alpha\sigma} + \frac{\lambda}{2} \sum_{i\alpha\beta} \sum_{\sigma\sigma'} \mathbf{L}_{\alpha\beta} \cdot [\sigma]_{\sigma\sigma'} d^\dagger_{i\alpha\sigma} d_{i\beta\sigma'}. \quad (4)$$

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 ion at site i. As in Ref. 16, 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 $|\,0\rangle$ is the lowest energy single–particle state. The second term in (4) is the spin-orbit interaction, with the matrix elements $\mathbf{L}_{\alpha\beta}$ of the orbital angular momentum. The unitary transformation that diagonalizes $\mathcal{H}_{\rm Cu}$ is given by[14,15]

$$d_{i\alpha\sigma} = \sum_{as} m_{\alpha a} [\sigma(\alpha)]_{\sigma s} c_{ias}, \quad (5)$$

where c_{ias} 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 a, and a pseudo-spin index s. In Eq. (5) we adopt the notation of Ref. 16 and define $\sigma(\alpha)$ for each crystal-field state $|\,\alpha\rangle$ as the Pauli matrix σ_α for $\alpha = x, y, z$, and $\sigma(\alpha) = I$ as the unit matrix for $\alpha = 0, 1$. The coefficients $m_{\alpha 0}$ which are needed to order $\mathcal{O}(\lambda)$ in the derivation of the magnetic Hamiltonian are[16] $m_{00} = 1$, $m_{10} = 0$, $m_{z0} = -i\lambda/\epsilon_z$, and $m_{x0} = m_{y0} = i\lambda/2\epsilon_x$.

The total Hamiltonian of the system,

$$\mathcal{H} = \mathcal{H}_{\rm Cu} + \mathcal{H}_{\rm O} + \mathcal{H}_{\rm hop} + \mathcal{H}_C^{\rm tot}, \quad (6)$$

in which $\mathcal{H}_{\rm O}$ describes the Hamiltonian of the oxygens, $\mathcal{H}_{\rm hop}$ is the kinetic energy due to hopping between Cu and O ions, and $\mathcal{H}_C^{\rm tot}$ contains the nonlocal Coulomb interactions, 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 (direct) Coulomb interaction between the copper 3d and oxygen 2p states,

$$\mathcal{H}_0 = \sum_{ias} E_a c^\dagger_{ias} c_{ias} + \sum_{kn\sigma} \tilde{\epsilon}_n p^\dagger_{kn\sigma} p_{kn\sigma} + \sum_{\substack{ikan\\ s\sigma}} U_{\rm pd}(anan) c^\dagger_{ias} p^\dagger_{kn\sigma} c_{ias} p_{kn\sigma}. \tag{7}$$

Here $p^\dagger_{kn\sigma}$ creates a hole in one of the three 2p orbitals (denoted by n) on the oxygen at site k. In the perturbation analysis, the Coulomb term $U_{\rm pd}$ only leads to a shift of the orbital energies of the oxygen, $\epsilon_n = \tilde{\epsilon}_n + U_{\rm pd}(0n0n)$.

The perturbation Hamiltonian $\mathcal{H}_1$ includes the kinetic energy and the general nonlocal Coulomb exchange interactions. Thus we have

$$\mathcal{H}_1 = \mathcal{H}_{\rm hop} + \mathcal{H}_C, \tag{8}$$

with the kinetic energy

$$\mathcal{H}_{\rm hop} = \sum_{ias} \sum_{kn\sigma} (\tilde{t}^{ik}_{an})_{s\sigma} c^\dagger_{ias} p_{kn\sigma} + \text{h.c.}, \tag{9}$$

in which due to the transformation (5) the hopping becomes spin-dependent and is given by a 2×2 matrix,

$$\tilde{t}^{ik}_{an} = \sum_\alpha t^{ik}_{\alpha n} m^*_{\alpha a} \sigma(\alpha) \ . \tag{10}$$

[For a list of the $t^{ik}_{\alpha n}$ *cf.* tables I and II of Ref. 16.] The Coulomb exchange interactions between the coppers,

$$\mathcal{H}_C^{(1)} = \sum_{\alpha\beta\gamma\delta} \sum_{ij\sigma\sigma'} V_{\alpha\beta\gamma\delta} d^\dagger_{i\alpha\sigma} d^\dagger_{j\beta\sigma'} d_{i\gamma\sigma'} d_{j\delta\sigma}, \tag{11}$$

together with the direct exchange between the neighboring copper and oxygen ions,

$$\mathcal{H}_C^{(2)} = \sum_{\alpha\beta mn} \sum_{ik\sigma\sigma'} K_{\alpha m\beta n} d^\dagger_{i\alpha\sigma} p^\dagger_{km\sigma'} d_{i\beta\sigma'} p_{kn\sigma}, \tag{12}$$

combine into $\mathcal{H}_C = \mathcal{H}_C^{(1)} + \mathcal{H}_C^{(2)}$, which describes the general nonlocal Coulomb exchange potentials,

$$\mathcal{H}_C = \sum_{ijabcd} \sum_{ss's_1s_1'} \bar{V}_{ss's_1s_1'}(abcd)\ c^\dagger_{ias} c^\dagger_{jbs'} c_{ics_1} c_{jds_1'} + \sum_{ikabmn} \sum_{ss'\sigma\sigma'} \bar{K}_{s\sigma's'\sigma}(ambn)\ c^\dagger_{ias} p^\dagger_{km\sigma'} c_{ibs'} p_{kn\sigma}. \tag{13}$$

The Coulomb matrix elements $\bar{V}_{ss's_1s_1'}(abcd)$ and $\bar{K}_{s\sigma's'\sigma}(ambn)$ are the matrix elements in the basis of the exact eigenstates of $\mathcal{H}_{\rm Cu}$,

$$\bar{V}_{ss's_1s_1'}(abcd) = \sum_{\alpha\beta\gamma\delta} m^*_{\alpha a} m^*_{\beta b} m_{\gamma c} m_{\delta d} \times V_{\alpha\beta\gamma\delta}\ [\sigma(\alpha)\sigma(\delta)]_{ss_1'} [\sigma(\beta)\sigma(\gamma)]_{s's_1}, \tag{14}$$

and

$$\bar{K}_{s\sigma's'\sigma}(ambn) = \sum_{\alpha\beta} m^*_{\alpha a} m_{\beta b} \times K_{\alpha m\beta n}\ [\sigma(\alpha)]_{s\sigma} [\sigma(\beta)]_{\sigma' s'}. \tag{15}$$

Note that due to the symmetry of the involved orbitals these matrix elements depend in general also on the direction of the bond. In (11) and (12) we have included all terms which in the perturbation analysis will enter into the magnetic anisotropies together with the leading orders in the copper-oxygen hopping. In principle, one could also consider even more general nonlocal Coulomb matrix elements, e.g., those generating (or destroying) two holes at a particular ion, or terms with equal spin indices at one site. In the perturbation expansion, however, such terms will enter with powers of the copper-oxygen hopping higher than the leading ones, or will not generate anisotropies, respectively. Some of the latter matrix elements [denoted by $U_{\rm pd}$ in (7)] are contained in $\mathcal{H}_0$, however.

The effective magnetic interaction $\mathcal{H}(i,j)$ between the magnetic ions i and j along a single bond is now obtained by a perturbation expansion with respect to $\mathcal{H}_1$. We consider separately the contributions which originate from the Coulomb exchange interactions between the coppers, $\mathcal{H}_C^{(1)}$, which we treat first, and those generated by the exchange between copper and oxygen, $\mathcal{H}_C^{(2)}$. The total magnetic interaction between a pair of copper ions,

$$\mathcal{H}(i,j) = \mathcal{H}^{(1)}(i,j) + \mathcal{H}^{(2)}(i,j), \tag{16}$$

is given by the sum of these contributions.

A. The Cu-Cu direct exchange

Since the new orbital eigenstates of the coppers [*cf.* Eq. (5)] already account for the effect of spin-orbit coupling, it is sufficient to consider the Coulomb interaction between holes in the new ground state $|0\rangle$ on the copper ions along a single bond. The contribution to the magnetic Hamiltonian due to the direct exchange between the Cu ions is then given by

$$\mathcal{H}^{(1)}(i,j) = \sum_{ss's_1s_1'} \bar{V}_{ss's_1s_1'}(0000) c^\dagger_{i0s} c^\dagger_{j0s'} c_{i0s_1} c_{j0s_1'}. \tag{17}$$

With the identification of the spin on the copper at site i in the orbital state $|0\rangle$ by

$$\mathbf{S}_i = \frac{1}{2} \sum_{ss'} c^\dagger_{i0s} (\sigma)_{ss'} c_{i0s'}, \tag{18}$$

one derives the spin interaction

$$\mathcal{H}^{(1)}(i,j) = -\sum_{\alpha\beta\gamma\delta} V_{\alpha\beta\gamma\delta} m^*_{\alpha 0} m^*_{\beta 0} m_{\gamma 0} m_{\delta 0} \times \mathrm{Tr}\Big\{(\sigma\cdot\mathbf{S}_i)\sigma(\alpha)\sigma(\delta)(\sigma\cdot\mathbf{S}_j)\sigma(\beta)\sigma(\gamma)\Big\}\ . \quad (19)$$

To obtain the coupling constants of the anisotropic magnetic Hamiltonian from this result, it is important to realize that the nonvanishing Coulomb terms $V_{\alpha\beta\gamma\delta}$, which involve tetragonal crystal-field states, obey symmetry requirements identical to those for the general *local* Coulomb matrix elements, which can be stated in the form[16,21]

$$\sigma(\alpha)\sigma(\delta) \sim \sigma(\beta)\sigma(\gamma). \quad (20)$$

This can be verified by inspecting the corresponding integrals and using the symmetry properties of the involved orbitals. Therefore, $\mathcal{H}^{(1)}(i,j)$ only contributes to the diagonal terms of the magnetic interaction tensor. After summation over the plaquette, these contribute only to the isotropic Heisenberg part of the effective magnetic Hamiltonian (1) and to the out-of-plane anisotropy Γ_z of the symmetric anisotropy tensor $\mathbf{\Gamma}$ [Eq. (2)].

B. The Cu-O direct exchange

We now consider the contributions to the magnetic Hamiltonian originating from the Coulomb exchange interaction between the nearest-neighbor copper and oxygen sites. These combine with hopping between copper and oxygen states, because first a hole has to be transferred from one copper ion to the adjacent oxygen to interact with the hole on the second copper. The perturbation expansion results in the expression

$$\mathcal{H}^{(2)}(i,j) = -\sum_{\alpha\gamma}\sum_{mn} \frac{K_{\alpha m\gamma n}}{\epsilon_m\epsilon_n} m^*_{\alpha 0} m_{\gamma 0} \times \mathrm{Tr}\Big\{(\sigma\cdot\mathbf{S}_i)\sigma(\alpha)\tilde{t}^{kj}_{n0}(\sigma\cdot\mathbf{S}_j)\tilde{t}^{jk}_{0m}\sigma(\gamma)\Big\}\ + (i\leftrightarrow j). \quad (21)$$

Inserting here the explicit form for $\tilde{t}$, Eq. (10), one obtains the magnetic interaction

$$\mathcal{H}^{(2)}(i,j) = -\sum_{\alpha\beta\gamma\delta}\sum_{mn} K_{\alpha m\gamma n}\frac{t^{jk}_{\beta m}t^{kj}_{n\delta}}{\epsilon_m\epsilon_n} m^*_{\alpha 0} m^*_{\beta 0} m_{\gamma 0} m_{\delta 0} \times \mathrm{Tr}\Big\{(\sigma\cdot\mathbf{S}_i)\sigma(\alpha)\sigma(\delta)(\sigma\cdot\mathbf{S}_j)\sigma(\beta)\sigma(\gamma)\Big\}\ + (i\leftrightarrow j). \quad (22)$$

Due to the tilting of the CuO_6 octahedra, the 2p orbitals of oxygen are rotated. In the basis $\{|p_x\rangle, |p_y\rangle, |p_z\rangle\}$ this rotation is represented by the matrix

$$\begin{aligned}\mathbf{U} &= \exp(\delta\mathbf{\Delta}) \\ &= \mathbf{1} + \mathbf{\Delta}\sin\delta + \mathbf{\Delta}^2(1-\cos\delta)\end{aligned} \quad (23)$$

with an antisymmetric generator $\mathbf{\Delta}$,

$$\mathbf{\Delta} = \begin{pmatrix} 0 & 0 & -\sin\alpha \\ 0 & 0 & \cos\alpha \\ \sin\alpha & -\cos\alpha & 0 \end{pmatrix}. \quad (24)$$

To obtain explicit expressions for the magnetic couplings of Eq. (1) the detailed forms of the hopping between the copper and oxygen ions, $t^{ik}_{\alpha m}t^{ki}_{n\beta}$, and of the Coulomb matrix elements $K_{\alpha m\gamma n}$ are required, both involving the rotated 2p orbitals on oxygen. We derive

$$\sum_{mn} K_{\alpha m\gamma n}\frac{t^{jk}_{\beta m}t^{kj}_{n\delta}}{\epsilon_m\epsilon_n} = \sum_{\substack{\tilde{m}'\tilde{n}' \\ \tilde{m}''\tilde{n}''}} \mathbf{R}_{\tilde{m}'\tilde{m}''}\mathbf{R}_{\tilde{n}''\tilde{n}'}\ K_{\alpha\tilde{m}'\gamma\tilde{n}'}\ t^{jk}_{\beta\tilde{m}''}t^{kj}_{\tilde{n}''\delta}, \quad (25)$$

with

$$\mathbf{R}_{\tilde{m}_1\tilde{m}_2} = \sum_m \frac{\mathbf{U}_{\tilde{m}_1 m}\mathbf{U}_{m\tilde{m}_2}}{\epsilon_m}. \quad (26)$$

In (25) the matrices $\mathbf{R}$ connect the unrotated oxygen 2p states of pure tetragonal symmetry (denoted by indices with a tilde).

We find that all nonvanishing Coulomb matrix elements $K_{\alpha\tilde{m}\beta\tilde{n}}$, which involve only the orbitals related to the undistorted tetragonal phase on both copper and oxygen, obey the symmetry relations $\sigma(\alpha)\sigma(\tilde{n}) \sim \sigma(\beta)\sigma(\tilde{m})$ analogous to Eq. (20). Here we use the notation $\sigma(m) = \sigma_m$, where σ_m is the Pauli matrix for the three oxygen 2p states ($m = x, y, z$). The nonzero hopping matrix elements $t^{ik}_{\alpha\tilde{m}}$ for a bond along the μ-direction ($\mu = x, y$) obey $\sigma(\alpha)\sigma(\tilde{m}) \sim \sigma_\mu$. Consequently, the possible spin anisotropies due to the exchange between the copper and the oxygen ions, as given by (22) and (25), are subject to a weaker constraint,

$$\sigma(\alpha)\sigma(\delta)\sigma(\tilde{n}')\sigma(\tilde{n}'') \sim \sigma(\beta)\sigma(\gamma)\sigma(\tilde{m}')\sigma(\tilde{m}''), \quad (27)$$

which allows for contributions to all couplings of the magnetic Hamiltonian (1). To see this more clearly, take for example $\sigma(\alpha)\sigma(\delta) \sim \sigma_x$ and $\sigma(\beta)\sigma(\gamma) \sim \sigma_y$. Such a term corresponds to a contribution to Γ_2 and would be excluded, if the constraint (20) had to be obeyed. Due to (27), however, with $\sigma(\tilde{n}')\sigma(\tilde{n}'') \sim \sigma_{x,y}$ and $\sigma(\tilde{m}')\sigma(\tilde{m}'') \sim \sigma_{y,x}$ this contribution does not vanish.

III. THE MAGNETIC COUPLING CONSTANTS

In this section we present the explicit results for the coupling constants of the effective planar magnetic Hamiltonian. Throughout this section it is understood that the nonlocal Coulomb matrix elements which in general depend on the direction of the bond are the ones for a bond along the $\hat{x}$-axis. As usual, we define $p_\sigma = p_x, p_\pi = p_y$ for a bond along $\hat{x}$, and $p_\sigma = p_y, p_\pi = p_x$ for a bond along $\hat{y}$. This notation is also applied to the copper states [e.g., $|\sigma\rangle = |x\rangle$ and $|\pi\rangle = |y\rangle$ for a bond along the $\hat{x}$-axis].

We first obtain the expression for the isotropic spin interaction, omitting contributions of order $\mathcal{O}(\lambda^2\delta^2)$ or higher,

$$J = -2\left(\frac{2t_0^2}{\epsilon_{p_\sigma}^2}K_{0p_\sigma 0p_\sigma} + V_{0000}\right). \tag{28}$$

This result corresponds to a ferromagnetic coupling of the Cu spins and reproduces the two contributions derived previously by Stechel and Jennison[17] and by Hanzawa,[20] respectively.

The out-of-plane anisotropy Γ_z is nonzero in the purely tetragonal phase and is found to leading order in the angle of rotation of the oxygen octahedra, $\mathcal{O}(\delta^0)$,

$$\begin{aligned}\Gamma_z = &-\frac{8\lambda^2}{\epsilon_z^2}\Big(V_{z0z0} - V_{zz00} + \frac{t_2^2}{\epsilon_{p_\pi}^2}K_{0p_\pi 0p_\pi}\\ &+\frac{t_0^2}{\epsilon_{p_\sigma}^2}K_{zp_\sigma zp_\sigma} + \frac{t_0t_2}{\epsilon_{p_\sigma}\epsilon_{p_\pi}}(K_{0p_\sigma zp_\pi} + K_{zp_\pi 0p_\sigma})\Big)\\ &+\frac{\lambda^2}{\epsilon_x^2}\Big(V_{\sigma 0\sigma 0} - V_{\sigma\sigma 00} + V_{\pi 0\pi 0} - V_{\pi\pi 00} + \frac{t_2^2}{\epsilon_{p_z}^2}K_{0p_z 0p_z}\\ &+\frac{t_0^2}{\epsilon_{p_\sigma}^2}(K_{\sigma p_\sigma \sigma p_\sigma} + K_{\pi p_\sigma \pi p_\sigma})\\ &+\frac{t_0t_2}{\epsilon_{p_\sigma}\epsilon_{p_z}}(K_{0p_\sigma \pi p_z} + K_{\pi p_z 0p_\sigma})\Big).\end{aligned} \tag{29}$$

The result for Γ_z obtained by Koshibae *et al.*[10] and by Hanzawa[20] is recovered from this more general expression by considering only the Coulomb matrix elements $V_{\mu 0\mu 0}$ (with $\mu = z, \sigma, \pi$).

The coupling constant D corresponding to the Dzyaloshinskii-Moriya interaction contains only contributions from the direct exchange between the copper and oxygen ions,

$$\begin{aligned}D = &\frac{t_0^2\lambda\delta}{2\epsilon_x\epsilon_{p_\sigma}}\Big(\frac{1}{\epsilon_{p_\sigma}} + \frac{1}{\epsilon_{p_z}}\Big)\\ &\times\Big((K_{0p_z yp_x} - K_{0p_x yp_z}) + (K_{yp_x 0p_z} - K_{yp_z 0p_x})\Big).\end{aligned} \tag{30}$$

The direct exchange between the coppers contributes to the diagonal terms of the symmetric anisotropy tensor in the effective magnetic Hamiltonian only in the leading order of the tilting angle, $\mathcal{O}(\delta^0)$, since the site symmetry of the copper is assumed to be tetragonal. Consequently, the coupling constant Γ contains only terms involving direct exchange between copper and oxygen sites,

$$\begin{aligned}\Gamma = &\frac{\lambda^2\delta^2}{\epsilon_x^2}\Big\{\Big(\frac{1}{\epsilon_{p_\sigma}} + \frac{1}{\epsilon_{p_z}}\Big)^2\Big(t_0^2(K_{\pi p_z \pi p_z} - K_{\sigma p_z \sigma p_z})\\ &+t_2^2(K_{0p_\sigma 0p_\sigma} - K_{0p_\pi 0p_\pi}) - t_0t_2(K_{0p_z \pi p_\sigma} + K_{\pi p_\sigma 0p_z})\Big)\\ &+\Big(\frac{1}{\epsilon_{p_\sigma}} + \frac{1}{\epsilon_{p_z}}\Big)\Big(\frac{2t_0^2}{\epsilon_{p_\sigma}}(K_{\pi p_\sigma \pi p_\sigma} - K_{\sigma p_\sigma \sigma p_\sigma})\\ &+\frac{t_0t_2}{\epsilon_{p_z}}(K_{0p_\sigma \pi p_z} + K_{\pi p_z 0p_\sigma})\Big) + \Big(\frac{1}{\epsilon_{p_\sigma}} - \frac{1}{\epsilon_{p_\pi}}\Big)\\ &\times\Big(\frac{2t_2^2}{\epsilon_{p_z}}K_{0p_z 0p_z} + \frac{t_0t_2}{\epsilon_{p_\sigma}}(K_{0p_\sigma \pi p_z} + K_{\pi p_z 0p_\sigma})\Big)\Big\}.\end{aligned} \tag{31}$$

Finally, we find the in-plane anisotropy

$$\begin{aligned}\Gamma_2 = &-\frac{2t_0^2\lambda^2\delta^2}{\epsilon_x^2\epsilon_{p_\sigma}}\left(\frac{1}{\epsilon_{p_z}} + \frac{1}{2}\Big(\frac{1}{\epsilon_{p_\sigma}} + \frac{1}{\epsilon_{p_\pi}}\Big)\right)\\ &\times(K_{\sigma p_\sigma \pi p_\pi} + K_{\sigma p_\pi \pi p_\sigma}).\end{aligned} \tag{32}$$

To estimate the numerical values of these coupling constants, we choose $U_{\mathrm{pd}} \simeq 2$ eV[17,22] and $K_{0p_\sigma 0p_\sigma} \simeq 0.2$ eV[17] for the largest nonlocal Coulomb matrix elements. The direct Coulomb exchange terms between the coppers are much smaller, e.g., $V_{0000} \simeq 1$ meV.[20] As in Ref. 16, we choose the spin-orbit coupling $\lambda = 0.1$ eV, the distortion of the octahedra $\delta = 0.05$, the copper-oxygen hopping $t_0 = 1.0$ eV, the crystal-field energies of copper $\epsilon_{3\mathrm{d}} = 1.0$ eV, and the orbital energies of oxygen $\tilde{\epsilon}_{p_\sigma} = 3$ eV, $\tilde{\epsilon}_{p_\pi} = \tilde{\epsilon}_{p_z} = 2$ eV. Due to the lack of more accurate values, we take all the Coulomb matrix elements between the copper and the oxygen to be equal to the largest one, $K_{0p_\sigma 0p_\sigma}$. Since in this approximation D would vanish, we allow for a finite value ($\simeq 0.05$ eV) for the differences of Coulomb matrix elements appearing in brackets in the corresponding expressions, (30) and (31). This choice of the Coulomb parameters may overestimate the values for the coupling constants quite considerably. We thus obtain the direct exchange contributions to the (ferromagnetic) isotropic spin interaction $J \simeq -30$ meV, the Dzyaloshinskii-Moriya coupling $D \simeq 0.02$ meV, and the symmetric anisotropy parameters $\Gamma \simeq -0.06$ μeV, $\Gamma_2 \simeq -2$ μeV, and $\Gamma_z \simeq -1$ meV.

Apart from Γ_z and Γ_2, these results are much smaller than the values obtained from the superexchange mechanism with purely local Coulomb interactions, which must be added to obtain the realistic magnetic coupling parameters. In comparison, the calculations in the framework of kinetic superexchange yield[16] $J \simeq 0.13$ eV, $D \simeq 1.1$ meV, $\Gamma \simeq 8.3$ μeV, $\Gamma_2 \simeq 0.43$ μeV, and $\Gamma_z \simeq -23$ μeV. In particular, the contributions to D and Γ, which are especially important for the magnetic properties of the ground state [*cf.* Eq. (15) of Ref. 16], are negligible compared to the leading superexchange terms. Therefore, we find that Coulomb direct exchange can be disregarded when studying the magnetic order in the ground state of the cuprates and the possibility of weak ferromagnetism.

Although our numerical estimates of the magnetic couplings should only be considered as an upper bound for the realistic values, the quite large result for Γ_z indicates that the direct exchange contributions to the out-of-plane anisotropy should not be neglected. However, more refined values for the nonlocal Coulomb matrix elements are required for its reliable evaluation.

IV. SUMMARY

In summary, we have studied the magnetic anisotropies in the copper-oxide planes due to the general Cu-Cu and Cu-O Coulomb direct exchange interactions and the spin-orbit coupling on the transition metal ions. Our calculations take into account the structural distortions in the low-temperature phases, and allow for a general rotation axis of the oxygen octahedra.

The anisotropic magnetic interaction resulting from the direct exchange mechanism exhibits a dependence on the structural properties of the cuprates which is identical to the one obtained within the framework of kinetic superexchange with purely local general Coulomb interactions.[16] As a particularly important result, the same dependence of the symmetric anisotropy tensor and of the Dzyaloshinskii-Moriya vector on the orientation of the tilting axis of the octahedra is found. Hence, the inclusion of Coulomb direct exchange interactions in the derivation of the effective spin couplings does not lead to qualitatively new magnetic anisotropies.

In addition, the numerical estimate for the coupling constants of the effective planar magnetic Hamiltonian yields that the contributions from the direct exchange interactions cannot affect qualitatively the magnetic order in the ground state. However, the contributions to the isotropic Heisenberg coupling and to the out-of-plane anisotropy should not be neglected. The latter may also give improved results for the spin-wave gaps. However, more important and fundamental than the numerical results may be the finding that both nonlocal and local general Coulomb interactions generate an identical form of the anisotropic magnetic Hamiltonian.

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