Bond-dependent symmetric and antisymmetric superexchange interactions in La_2CuO_4

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The effective spin Hamiltonian that describes the magnetic properties of La_2CuO_4 is derived from the nearest-neighbor superexchange interactions. It is shown that the spin system of the CuO_2 plane of the compound is frustrated; the principal axes of the symmetric parts of the one-bond anisotropy tensors are not the same for all the bonds. We also show that, due to a hidden symmetry of the one-bond anisotropic superexchange interactions, the symmetry of the lattice alone leads to the identification of the largest eigenvalue of the mean-field superexchange anisotropy tensor. The derived mean-field spin Hamiltonian is identical to that used previously on a phenomenological basis to account for the magnetic properties of La_2CuO_4 in the orthorhombic phase. Similar arguments explain the magnetic structure in the low-temperature tetragonal phase. These structures cannot be obtained without the inclusion of the symmetric part of the anisotropy tensor, neglected in other papers. Finally, we show how the addition of direct exchange may explain the observed spin-wave gaps.

I. INTRODUCTION

The phase diagrams of all the lamellar copper oxide superconductors contain an antiferromagnetic phase in the vicinity of the superconducting one.[1] This led to the idea that magnetism is the progenitor of high-temperature superconductivity, serving as a basis for many recent theoretical models. To understand better the hopping of holes or electrons in the CuO_2 planes, one needs to understand the magnetic structure and magnetic interactions in these planes. Much of the study of these magnetic properties has been carried out on undoped La_2CuO_4, which becomes superconducting upon doping.[2]

Although the two-dimensional $S=\frac{1}{2}$ Heisenberg antiferromagnet is a good approximation for La_2CuO_4, experiments have shown small gaps in the spin-wave spectrum[3] and a finite ferromagnetic moment of each plane, due to canting of the spins out of the plane.[4] Both of these have been attributed to an antisymmetric[5,6] "Dzyaloshinsky-Moriya" (DM) superexchange interaction.

The most general effective spin Hamiltonian describing the nearest-neighbor interaction between Cu spins may be written in the form

$$H_s=\sum_{\langle kl\rangle}\{J_{kl}\mathbf{S}_k\cdot\mathbf{S}_l+\mathbf{D}_{kl}\cdot\mathbf{S}_k\times\mathbf{S}_l+\mathbf{S}_k\cdot\overleftrightarrow{A}_{kl}\cdot\mathbf{S}_l\}\ . \tag{1.1}$$

The first term represents the isotropic symmetric exchange, and it is commonly agreed that $J_{kl}=J$ has the same value for all nearest-neighbor Cu-Cu bonds in the CuO_2 plane. The second and the third terms represent the antisymmetric ($\mathbf{D}_{kl}=-\mathbf{D}_{lk}$) and symmetric ($\overleftrightarrow{A}_{kl}=\overleftrightarrow{A}_{lk}$) anisotropies. Coffey and co-workers[7,8] emphasized that in general the one-bond vectors $\mathbf{D}_{kl}$ cannot be the same for all the bonds. The relations between various $\mathbf{D}_{kl}$'s are not arbitrary. These relations are determined by the symmetry transformations, allowed under the given crystalline structure. Coffey, Rice, and Zhang[9] appended the symmetry analysis of Ref. 7 with microscopic calculations of the vectors $\mathbf{D}_{kl}$ ("Moriya vectors" below) in the framework of the Moriya[6] theory of the anisotropic superexchange interactions. They followed Moriya[6] in assuming that the antisymmetric anisotropy $\mathbf{D}_{kl}$ is the leading anisotropy, because $|\mathbf{D}_{kl}|\sim(\Delta g/g)J$ while $|\overleftrightarrow{A}_{kl}|\sim(\Delta g/g)^2J$, where Δg is a shift in the value of the free-electron gyromagnetic ratio g due to the spin-orbit interaction. With this assumption they derived an expression for the Dzyaloshinsky-Moriya interaction concentrating only on $\mathbf{D}_{kl}$, and disregarding $\overleftrightarrow{A}_{kl}$.

Recently,[10] we followed Moriya's derivation of the anisotropic superexchange contribution to Eq. (1.1) from the Hubbard Hamiltonian for hopping between the sites k and l, and showed that the tensors $\overleftrightarrow{A}_{kl}$ can *never* be neglected. We stressed that, generally, both $\mathbf{D}_{kl}$ and $\overleftrightarrow{A}_{kl}$ may vary from bond to bond. However, for each bond $\overleftrightarrow{A}_{kl}$ and $\mathbf{D}_{kl}$ are not independent; they are related to each other in such a way that a rotation of the spin axes on k and l maps the single-bond Hamiltonian onto an isotropic one, $\mathbf{S}'_k\cdot\mathbf{S}'_l$, with no preferred direction of the staggered magnetization. This hidden degeneracy results from an exact cancellation of terms of order $(\mathbf{D}_{kl})^2$ and $J\cdot\overleftrightarrow{A}_{kl}$, which is related to an invariance of the original hopping Hamiltonian under a gauge transformation.[10] We further showed that this degeneracy persists for the whole lattice if there is no frustration among the spin rotations required on the individual bonds. This happens only if the Moriya vectors $\mathbf{D}_{kl}$'s point along special directions, so that the tensors $\overleftrightarrow{A}_{kl}$ become bond independent.

The classical ground state of Eq. (1.1) is easily discussed in the case when the spins order in two sublattices, so that all the neighbors of each spin belong to the other sublattice. In this case, Eq. (1.1) may be reduced to the energy

$$F=J\mathbf{M}_1\cdot\mathbf{M}_2+\mathbf{D}^D\cdot\mathbf{M}_1\times\mathbf{M}_2+\mathbf{M}_1\cdot\overleftrightarrow{A}\cdot\mathbf{M}_2\ , \tag{1.2}$$

where $\mathbf{M}_1$ and $\mathbf{M}_2$ are the two sublattice magnetizations and $\mathbf{D}^D$ is the Dzyaloshinsky[5] vector. For this special

case, one has[10,11]

$$\mathbf{D}^D=\frac{1}{N_0}\sum_l \mathbf{D}_{kl} , \tag{1.3}$$

$$\overleftrightarrow{A}=\frac{1}{N_0}\sum_l \overleftrightarrow{A}_{kl} , \tag{1.4}$$

where k belongs to sublattice 1, and the sums are over its N_0 nearest neighbors (which belong to sublattice 2).

In the present paper we identify microscopically the macroscopic anisotropy parameters $\mathbf{D}^D$ and $\overleftrightarrow{A}$ for the low-temperature orthorhombic (LTO) phase of La_2CuO_4, investigate the corresponding classical ground-state spin configuration, and compare it with that of the low-temperature tetragonal (LTT) (Refs. 9 and 12) phase of the compound. Our results are summarized as follows: (a) For the lattice symmetry of the LTO phase, Eq. (1.2) yields no ferromagnetic moment only in one of two cases, i.e., when $\mathbf{D}_{kl}$ points along the orthorhombic $\hat{a}$ or $\hat{c}$ axes. In all other cases, there is a definite weak ferromagnetic moment and the ground state is uniquely determined by superexchange alone. *Derived* from superexchange, $\mathbf{D}_{kl}$ has almost equal $\hat{a}$ and $\hat{c}$ components. Hence, $\overleftrightarrow{A}_{kl}$ depends on the bonds and superexchange is sufficient to explain the weak ferromagnetism of the LTO phase. (b) The classical superexchange ground-state spin configuration of the LTT phase is always purely antiferromagnetic. This is in contrast with the weakly ferromagnetic ground state resulting in the approach of Coffey, Rice, and Zhang.[9] (c) Due to the hidden single-bond symmetry of the superexchange interaction, symmetry arguments alone are sufficient to show that the ground state has only two sublattices, and to identify the direction of the antiferromagnetic moment and of the weak ferromagnetic moment. (d) The superexchange interaction in an isolated CuO_2 plane *cannot account in principle* for the observable difference of the in-plane and out-of-plane gaps in the spin-wave spectra.[3] For all quasiplanar systems (without an interplane Dzyaloshinsky-Moriya coupling) the superexchange contributions to the two gaps are exactly equal to one another. This "residual" symmetry of the superexchange, which survives under frustration, is broken by the direct exchange interaction. (e) At the level of a classical mean-field theory, one recovers the phenomenological model of Thio *et al.*,[4] provided that one replaces the "Dzyaloshinsky-Moriya vector" in their expressions by the absolute value of the component of the microscopic Moriya vector along the $\hat{a}$ axis. This results from Eq. (1.3), in which (combined with the symmetry of the orthorhombic La_2CuO_4) all the $\hat{c}$ components of the $\mathbf{D}_{kl}$'s cancel. It would be very interesting to consider new experiments, e.g., with magnetic fields in general directions or with microscopic local probes, to check our predictions concerning the other components of $\mathbf{D}_{kl}$ and the details of the tensors $\overleftrightarrow{A}_{kl}$.

In outline, we start in Sec. II with a derivation of the spin Hamiltonian for the CuO_2 plane of La_2CuO_4. In Sec. III we establish the relation between the microscopic spin Hamiltonian and the mean-field anisotropies and investigate the classical ordered state assuming that it can be discussed in terms of two interpenetrating magnetic sublattices. Section IV is devoted to the justification of the assumptions about the symmetry relations between the various one-bond anisotropy tensors employed in Sec. III. In Sec. V we discuss the role of the direct exchange interaction. Details of the symmetry arguments are given in Appendix A, estimates of the magnitudes of the matrix elements are discussed in Appendix B, and Appendix C is devoted to the determination of the leading-order direct exchange contribution to the spin Hamiltonian of the orthorhombic La_2CuO_4.

II. DERIVATION OF THE SPIN HAMILTONIAN

We start with the Hubbard Hamiltonian, describing the hopping and the interactions of the holes residing in the CuO_2 plane of La_2CuO_4 (see Fig. 1). It includes copper $3d_{x^2-y^2}$ and oxygen $2p_{x,y}$ orbitals (represented, respectively, by the creation operators $d_{i\sigma}^\dagger$ and $p_{i\sigma}^\dagger$ for site i and spin σ) and the copper on-site Coulomb correlation, U. It is convenient to separate the Hamiltonian H into the on-site part H_0 and the hopping part H_1,

$$H=H_0+H_1 , \tag{2.1}$$

$$H_0=\epsilon_d\sum_{k\sigma} d_{k\sigma}^\dagger d_{k\sigma}+\epsilon_p\sum_{i\sigma} p_{i\sigma}^\dagger p_{i\sigma}+U\sum_k n_{k\uparrow}^d n_{k\downarrow}^d , \tag{2.2}$$

$$H_1=\sum_{\langle ki\rangle}\sum_{\sigma\sigma'} t_{ki}^{\sigma\sigma'} d_{k\sigma}^\dagger p_{i\sigma'}+\text{H.c.} , \tag{2.3}$$

with $n_{k\sigma}^d=d_{k\sigma}^\dagger d_{k\sigma}$.

The calculation of the hopping matrix elements $t_{ki}^{\sigma\sigma'}$ involves two steps.[6] First, the on-site spin-orbit coupling mixes excited crystal levels (m) into the ground states (0) of the Cu and O ions. These renormalized ground states are then used to calculate the hopping between neighboring Cu and O ions. The latter calculation also involves inter-ion spin-orbit terms. The resulting 2×2 matrix (in spin space) may be written in the general form

$$t_{ki}=\hat{t}_{ki}\overleftrightarrow{I}+i\mathbf{t}_{ki}\cdot\boldsymbol{\sigma} , \tag{2.4}$$

where $\boldsymbol{\sigma}$ represents the Pauli matrices and $\overleftrightarrow{I}$ is the unit

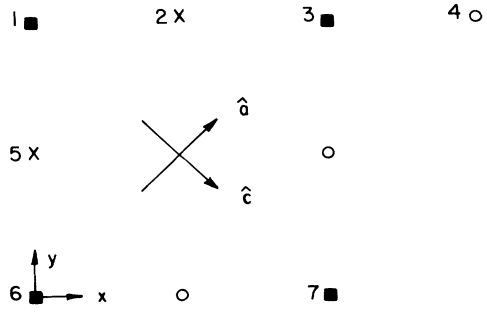

FIG. 1. CuO_2 plane of La_2CuO_4. The squares represent Cu ions, the crosses (circles) are oxygen ions, which in the orthorhombic phase are tilted down (up) out of the plane. The vectors $\hat{a}$ and $\hat{c}$ denote the orthorhombic axes.

matrix. It was shown by Moriya[6] that

$$\mathbf{t}_{ki}=-\frac{1}{2}\lambda_{\mathrm{Cu}}\sum_m \frac{(\mathbf{L}^d_{m0})^*}{\epsilon^d_m-\epsilon^d_0}\hat{t}_{ki}(d_m,p_0) -\frac{1}{2}\lambda_O\sum_m \frac{\mathbf{L}^p_{m,0}}{\epsilon^p_m-\epsilon^p_O}\hat{t}_{ki}(d_0,p_m)+\mathbf{c}_{ki} , \tag{2.5}$$

where

$$\hat{t}_{ki}(d_m,p_0)=\langle \phi^d_{km}|V|\phi^p_{i0}\rangle , \tag{2.6}$$

and

$$\mathbf{c}_{ki}=\frac{\hbar}{4m^2c^2}\langle \phi^d_{k0}|\nabla V\times\mathbf{p}|\phi^p_{i0}\rangle . \tag{2.7}$$

Here $\mathbf{L}^d_{m0}$ and $\mathbf{L}^p_{m0}$ are the matrix elements of the angular momentum, λ_{Cu} and λ_{O} are the strengths of the spin-orbit coupling for Cu and O, respectively, and V is the tight-binding perturbation part of the crystal potential.

In the undoped case (i.e., one hole per unit cell) the Hamiltonian [Eqs. (2.1)–(2.3)] can be mapped[6,13] onto a spin Hamiltonian of the form of Eq.(1.1), with spin degrees of freedom on the Cu sites. This was the approach taken by Coffey, Rice, and Zhang.[9] We repeat the procedure here in order to include in the resulting spin Hamiltonian the symmetric anisotropy terms neglected by them.

Consider the undoped La_2CuO_4. To derive the spin Hamiltonian describing an effective interaction between the Cu^{2+} spins, we assume that

$$|t^{\sigma\sigma'}_{ki}|\ll\{U-\Delta,\Delta\} , \tag{2.8}$$

where $\Delta=\epsilon_d-\epsilon_p$, and treat H_1 [Eq. (2.3)] as a perturbation. In the ground state of H_0 [Eq. (2.2)] each Cu ion is occupied by one hole and each O ion has no holes. This state is highly degenerate, due to the absence of correlations between the orientations of the hole spins occupying neighboring Cu ions. The perturbation lifts this degeneracy. The lowest-order [$O(t^4)$] spin-dependent contribution arises from virtual excited states in which two holes reside on the same ion. The resulting effective spin Hamiltonian is thus

$$H_s=-\frac{1}{\Delta^2U}P_0H_1P_pH_1P_{2d}H_1P_pH_1P_0 -\frac{1}{2\Delta^3}P_0H_1P_pH_1P_{2p}H_1P_pH_1P_0 , \tag{2.9}$$

where P_0, P_p, P_{2p}, and P_{2d} are projection operators onto the ground state, the state with one empty Cu and one occupied O ion, the state with one doubly occupied O and two empty Cu sites, and the state with one doubly occupied Cu and one empty Cu ion, respectively.

Defining

$$\tilde{d}_{k\sigma}=d_{k\sigma}(1-n_{k-\sigma}),\quad \hat{d}_{k\sigma}=d_{k\sigma}n_{k-\sigma} , \tag{2.10}$$

and similarly $\tilde{p}_{i\sigma}$ and $\hat{p}_{i\sigma}$, we have

$$P_0H_1P_p=\sum_{\langle ki\rangle}t^{\sigma\sigma'}_{ki}\tilde{d}^\dagger_{k\sigma}\tilde{p}_{i\sigma'} ,$$
$$P_pH_1P_{2p}=\sum_{\langle ki\rangle}t^{\sigma\sigma'}_{ki}\tilde{d}^\dagger_{k\sigma}\hat{p}_{i\sigma'} , \tag{2.11}$$
$$P_{2d}H_1P_p=\sum_{\langle ki\rangle}t^{\sigma\sigma'}_{ki}\hat{d}^\dagger_{k\sigma}\tilde{p}_{i\sigma'} .$$

Using $\mathbf{S}_k=d^\dagger_k\boldsymbol{\sigma}d_k$, Eq. (2.9) can be rewritten in the form (1.1) with

$$J_{kl}\equiv J=2Kt^4 , \tag{2.12}$$

$$\mathbf{D}_{kl}=8Kt^2\mathbf{B}_{kl} , \tag{2.13}$$

$$A^{zz}_{kl}=-8K[(B^x_{kl})^2+(B^y_{kl})^2] ,$$
$$A^{xx}_{kl}=-A^{yy}_{kl}=8K[(B^x_{kl})^2-(B^y_{kl})^2] , \tag{2.14}$$
$$A^{xy}_{kl}=A^{yx}_{kl}=16KB^x_{kl}B^y_{kl} ,$$
$$A^{xz}_{kl}=A^{yz}_{kl}=A^{zx}_{kl}=A^{zy}_{kl}=0 .$$

Here

$$K=\frac{1}{2\Delta^3}+\frac{1}{\Delta^2U} , \tag{2.15}$$

and

$$t^2=\hat{t}^2+(t^z)^2-(t^x)^2-(t^y)^2 \tag{2.16}$$

are independent of the bonds ($\hat{t}$ and $\mathbf{t}$ can be taken from any Cu-O bond). The vector $\mathbf{B}_{kl}$ is given by

$$B^x_{kl}=t^y_{ki}t^z_{ki}-\hat{t}_{ki}t^x_{ki} ,$$
$$B^y_{kl}=-t^x_{ki}t^z_{ki}-\hat{t}_{ki}t^y_{ki},\quad B^z_{kl}=0 , \tag{2.17}$$

where i represents the oxygen which resides on the bond $\langle kl\rangle$. Note that $\mathbf{D}_{kl}$ and $A^{\alpha\beta}_{kl}$, with $\alpha,\beta=x,y$, have a nontrivial dependence on the specific bond.

Taking into account that [cf. Eqs. (2.13) and (2.14)]

$$4JA^{xx}_{kl}=-4JA^{yy}_{kl}=(D^x_{kl})^2-(D^y_{kl})^2 ,$$
$$4JA^{zz}_{kl}=-|\mathbf{D}_{kl}|^2,\quad 2JA^{xy}_{kl}=D^x_{kl}D^y_{kl} , \tag{2.18}$$

it is possible to rewrite the superexchange one-bond part of Eq. (1.1) in the form

$$H_{kl}=\left[J_{kl}-\frac{|\mathbf{D}_{kl}|^2}{4J_{kl}}\right]\mathbf{S}_k\cdot\mathbf{S}_l +\mathbf{D}_{kl}\cdot\mathbf{S}_k\times\mathbf{S}_l+\frac{1}{2J_{kl}}\mathbf{S}_k\cdot\mathbf{D}_{kl}\mathbf{D}_{kl}\cdot\mathbf{S}_l , \tag{2.19}$$

where $\mathbf{D}_{kl}\mathbf{D}_{kl}$ is a diadic. We stress (see Ref. 10) that the two-spin ground state of the Hamiltonian (2.19) is as degenerate as that of the Heisenberg Hamiltonian describing the isotropic exchange. Indeed, expression (2.19) is just the scalar product[10] of two spins, $\mathbf{S}'_k$ and $\mathbf{S}'_l$, obtained from the original ones by rotations around the $\mathbf{D}_{kl}$ axis with angles $-\theta$ and θ, respectively, where $\tan\theta=|\mathbf{D}_{kl}|/2J_{kl}$.

III. THE ORDERED STATE

We next turn to the superexchange spin Hamiltonian for the entire CuO_2 plane. Let us assume that (see Fig. 1) for the bonds in $\hat{x}$ direction $\mathbf{D}_{kl}=\pm\mathbf{D}_1$ and for those in $\hat{y}$ direction $\mathbf{D}_{kl}=\pm\mathbf{D}_2$, where $\mathbf{D}_{1,2}=\mathbf{D}_{67,61}$. Clearly, this is true in all the situations when the plane can be constructed from the plaquettes depicted on Fig. 1. Assume also (see Sec. IV and Refs. 7 and 9) that the $\mathbf{D}_{kl}$'s alternate their sign from bond to bond along a straight line and that the ground-state spin configuration and the low-lying excitations can be described in terms of the magnetizations of two interpenetrating sublattices. All these assumptions will be justified in Sec. IV. With these assumptions, the Dzyaloshinsky vector $\mathbf{D}^D$ and the macroscopic anisotropy tensor $\overleftrightarrow{A}$ [see Eqs. (1.3) and (1.4)] can be written as

$$\overleftrightarrow{A}=-\frac{1}{4J}(|\mathbf{D}^+|^2+|\mathbf{D}^-|^2)\cdot\overleftrightarrow{I}+\frac{1}{2J}(\mathbf{D}^+\mathbf{D}^+ +\mathbf{D}^-\mathbf{D}^-)\ ,$$
$$\mathbf{D}^D\equiv\mathbf{D}^+\ , \tag{3.1}$$

where $\mathbf{D}^{\pm}=\frac{1}{2}(\mathbf{D}_1\pm\mathbf{D}_2)$. The expression Eq. (1.2) for the free energy takes the form

$$F=\left[J-\frac{|\mathbf{D}^+|^2}{4J}\right]\mathbf{M}_1\cdot\mathbf{M}_2+\mathbf{D}^+\cdot\mathbf{M}_1\times\mathbf{M}_2$$
$$+\frac{1}{2J}\mathbf{M}_1\cdot\mathbf{D}^+\mathbf{D}^+\cdot\mathbf{M}_2$$
$$-\frac{|\mathbf{D}^-|^2}{4J}\mathbf{M}_1\cdot\mathbf{M}_2+\frac{1}{2J}\mathbf{M}_1\cdot\mathbf{D}^-\mathbf{D}^-\cdot\mathbf{M}_2\ . \tag{3.2}$$

Let us decompose the free-energy Eq. (3.2) onto two parts. The first part (F^+) corresponds to the first two lines of Eq. (3.2) and does not depend on $\mathbf{D}^-$. The second part (F^-) contains the contribution from $\mathbf{D}^-$. When $\mathbf{D}^-=0$, $F=F^+$ becomes exactly of the form of Eq. (2.19). Therefore, it can be mapped onto an isotropic spin Hamiltonian, by appropriate unfrustrated rotations of $\mathbf{M}_1$ and $\mathbf{M}_2$. In this case the classical ground-state configuration is as degenerate as that of the one-bond superexchange Hamiltonian, and cannot be characterized by any definite net ferromagnetic moment.[10] In this ground state the vector of staggered magnetization $\mathbf{M}^{\dagger}=\frac{1}{2}(\mathbf{M}_1-\mathbf{M}_2)$ is free to point along any direction in space. The largest net ferromagnetic moment arises when $\mathbf{M}^{\dagger}$ is perpendicular to the Dzyaloshinsky vector $\mathbf{D}^+$, while the state with $\mathbf{M}^{\dagger}\|\mathbf{D}^{\dagger}$ is completely antiferromagnetic.[10] A nonzero $\mathbf{D}^-$ breaks this (hidden) symmetry and picks as the ground state the configuration with $\mathbf{M}^{\dagger}$ parallel to the (antiferromagnetic) easy axis of F^-, which in turn is parallel to $\mathbf{D}^-$ [see Eq. (3.2)]. Clearly, the directions of the vectors $\mathbf{D}^{\pm}$ are unambiguously defined by the symmetry of the given crystalline structure. Thus the superexchange interaction provides us with an example of an unusual situation, when symmetry analysis *alone* allows not only the classification of the possible ground states according to the symmetry group irreducible representations, but also to predict which of the representations yields the lowest energy. We conclude that under frustration ($\mathbf{D}^-\neq 0$) the staggered magnetization of the ground state is directed along $\mathbf{D}^-$ and the net ferromagnetic moment is proportional to $\mathbf{D}^-\times\mathbf{D}^+$. This statement may also be verified directly by minimizing the free-energy Eq. (3.2) with respect to the staggered magnetization and the net ferromagnetic moment.

These predictions are quite different from those based on Moriya's statement that the antisymmetric anisotropy is the leading order. Indeed, neglecting the symmetric anisotropy (see, e.g., Ref. 9) we would find that the staggered magnetization always lies in the plane perpendicular to $\mathbf{D}^+$, and that the role of the symmetric anisotropies is to fix its direction in this plane. We would also find that a nonzero $\mathbf{D}^+$ always leads to a nonzero net ferromagnetic moment. Thus in the framework of such an approach $\mathbf{D}^+$ is the only relevant vector and $\mathbf{D}^-$ does not play any qualitatively important role. In this sense we would not be able to differentiate between the LTO and LTT phases of La_2CuO_4, because in both cases $\mathbf{D}^+$ is nonzero. Thus the approach taken by Coffey, Rice and Zhang[9] predicts *in both cases* (and not only in that of LTO as is stated in Ref. 9) a weak ferromagnetic ground state with the spins ordered in the plane perpendicular to the Dzyaloshinsky vector.

In fact, the classical superexchange ground-state spin configurations of the LTO and LTT phases are indeed different: only that of the LTO phase is weakly ferromagnetic. This follows from the fact (see also Ref. 9 and Sec. IV) that the symmetry of the LTO phase confines the vectors $\mathbf{D}_{1,2}$ to be of the same *magnitude*, while the symmetry of the LTT phase implies that $\mathbf{D}_1$ and $\mathbf{D}_2$ point along the same *direction*. Thus in the LTO phase $\mathbf{D}^+\perp\mathbf{D}^-$, while in the LTT phase $\mathbf{D}^+\|\mathbf{D}^-$. Recalling our results we conclude that in the LTT phase the spins in the classical ground-state spin configuration are ordered *completely antiferromagnetically* along the Dzyaloshinsky vector $\mathbf{D}^+$, because $\mathbf{D}^+\times\mathbf{D}^-\equiv 0$, while in the LTO phase the vector $\mathbf{D}^+\times\mathbf{D}^-$ is generally nonzero, leading to weak ferromagnetism. Let us stress once again that in order to come to this conclusion one must take into account the symmetric part of the superexchange anisotropy tensor, neglected by Coffey, Rice, and Zhang.[9]

The above discussion implies that the only two special cases when the theory of superexchange does not predict a nonzero net ferromagnetic moment in the classical ground-state configuration of the LTO phase are those in which either the "vector of frustration" $\mathbf{D}^-$ or the Dzyaloshinsky vector $\mathbf{D}^+$ vanishes. By the definition of these vectors, this would happen only if all the $\mathbf{D}_{kl}$'s in the LTO phase were not only of the same magnitude but also aligned along the same direction ($\mathbf{D}_1=\pm\mathbf{D}_2$). This condition is equivalent to that of the bond independence of the $\overleftrightarrow{A}_{kl}$'s [see Eq. (2.19)]. We have already pointed out that, if $\mathbf{D}^-=0$, then the ground state is as degenerate as that of the one-bond Hamiltonian Eq. (2.19). This degeneracy leads to gapless spin-wave spectra, contrary to the assumption of Coffey, Bedell, and Trugman,[7] that in this case the Dzyaloshinsky-Moriya interaction produces an easy plane anisotropy. In the case $\mathbf{D}^+=0$, the Dzyaloshinsky vector vanishes and [see Eq. (3.2)] the classical ground-state spin configuration is completely antiferro-

magnetic. In Appendix B we show that, in fact, in the LTO phase each $\mathbf{D}_{kl}$ is almost perpendicular to the corresponding bond $\langle kl \rangle$. Hence, $\mathbf{D}_1$ and $\mathbf{D}_2$ are almost perpendicular to each other, and the vectors $\mathbf{D}^+$ and $\mathbf{D}^-$ are *both* nonzero and perpendicular to each other. Only due to this fact is it possible to explain[3,4] the experimentally observed properties of La_2CuO_4 on the basis of the theory of anisotropic superexchange interactions.

IV. THE LOW-TEMPERATURE ORTHORHOMBIC PHASE.

This section is devoted to the justification of the assumptions employed in Sec. III for the case of the LTO phase, and can be skipped by a reader uninterested in technical details. In order to show that the various $\mathbf{D}_{kl}$'s are indeed related to each other as was assumed in Sec. III, we first apply symmetry considerations to the various $\hat{t}_{ki}$ and $\mathbf{t}_{ki}$. In the LTO phase, the lattice of La_2CuO_4 is orthorhombically distorted[14] as a result of a small staggered rotation of the CuO_6 octahedra around the $\hat{a}$ axis (Fig. 1). Alternate rows of oxygen ions, parallel to this axis, move up and down (crosses and circles in Fig. 1) relative to the CuO_2 plane. As a result of this rotation, the inversion symmetry about the in-plane oxygen site, which prevails in the tetragonal phase, is lost. This gives rise to the Dzyaloshinsky term [see Eq. (1.2)] in the effective spin Hamiltonian.[5] Using rotations, reflections, and inversions, we show in Appendix A that (the site notations are those of Fig. 1)

$$\hat{t}_{12}=-\hat{t}_{32}=\hat{t}_{15}=\hat{t}_{34} , \tag{4.1}$$

$$t^{x,y}_{12}=t^{x,y}_{32}=t^{y,x}_{15}=-t^{x,y}_{34} , \tag{4.2}$$

$$t^{z}_{12}=-t^{z}_{32}=-t^{z}_{15}=t^{z}_{34} . \tag{4.3}$$

We also show in Appendix A that t^x and t^y are odd, while $\hat{t}$ and t^z are even functions of θ, the rotation angle of the octahedra. To leading order, $\hat{t}\sim\theta^0$, $t^{x,y}\sim\theta$, and $t^z\sim\theta^2$.

It follows from Eqs. (2.13), (2.17), and (4.1)–(4.3) that (see also Refs. 7 and 9)

$$\mathbf{D}_{67}=\mathbf{D}_{13}=\mathbf{D}_1,\quad \mathbf{D}_{61}=\mathbf{D}_{73}=\mathbf{D}_2 , \tag{4.4}$$

$$D^x_1=D^y_2,\quad D^y_1=D^x_2,\quad D^z_1=D^z_2=0 . \tag{4.5}$$

The fact that the relations Eqs. (4.4) and (4.5) hold for each plaquette leads to the conclusion that all the $\mathbf{D}_{kl}$'s can be constructed from $\mathbf{D}_{1,2}$ just as it was assumed in Sec. III. It also follows from Eq. (4.5) that $|\mathbf{D}_1|=|\mathbf{D}_2|$, meaning that in the LTO phase $\mathbf{D}^+$ is indeed perpendicular to $\mathbf{D}^-$. Moreover, Eq. (4.5) shows that $\mathbf{D}^+$ is directed along the orthorhombic $\hat{a}$ axis while $\mathbf{D}^-\|\hat{c}$.

Let us discuss next the validity of our assumption that the classical ground-state spin configuration of the copper oxide planes and the corresponding low-lying excitations can be described in terms of two interpenetrating sublattice magnetizations. We first note that the classical ground-state energy (per spin) of the spin system on the lattice is higher than or equal to that of a cluster consisting of a finite number of the lattice elementary cells. Equality is reached only when one can construct a lattice spin configuration by translations of this supercell, i.e., when the cluster ground-state spin configuration does not frustrate the translations. The magnetic elementary cell is represented by the smallest supercell possible in this sense.

Clearly, the one-, two- and three-bond clusters do not satisfy this condition, because the corresponding spin systems are not frustrated (the corresponding graphs are not closed). Indeed, in these cases the frustration associated with the bond dependence of the anisotropy parameters will enter the problem by frustrating not the cluster spin system, but rather the lattice construction from the corresponding supercells. The smallest cluster with the spin system as frustrated as the entire system is the four-bond one, corresponding to the plaquette (see Fig. 1) $\mathbf{S}_1$, $\mathbf{S}_3$, $\mathbf{S}_6$, and $\mathbf{S}_7$. In what follows, we shall show that its ground state is translationally invariant, and therefore corresponds to the ground state of the whole system. Thus, analyzing the ordering of the plaquette spins enables us to determine the number of sublattices.

Considering the plaquette, we start by rotating the spin coordinates into the orthorhombic directions. In these coordinates

$$\begin{aligned} &D^c_{13}=D^c_{37}=D^c_{76}=D^c_{61}\equiv D^c,\quad D^b_{kl}\equiv 0 ,\\ &D^a_{13}=-D^a_{37}=D^a_{76}=-D^a_{61}\equiv D^a ,\\ &J^{ac}_{13}=-J^{ac}_{37}=J^{ac}_{76}=-J^{ac}_{61}\equiv J^{ac} ,\\ &J^{\alpha\alpha}_{12}=J^{\alpha\alpha}_{37}=J^{\alpha\alpha}_{76}=J^{\alpha\alpha}_{61}\equiv J^{\alpha\alpha},\quad \alpha=a,b,c, \end{aligned} \tag{4.6a}$$

where

$$\begin{aligned} &J^{aa}=J+A^{xy}_{kl}=J+\frac{(D^a)^2-(D^c)^2}{4J} ,\\ &J^{bb}=J+A^{zz}_{kl}=J-\frac{|\mathbf{D}|^2}{4J} ,\\ &J^{cc}=J-A^{xy}_{kl}=J-\frac{(D^a)^2-(D^c)^2}{4J} \end{aligned} \tag{4.6b}$$

are bond independent, and

$$J^{ac}_{kl}=A^{xx}_{kl} . \tag{4.6c}$$

Introducing the notations

$$\mathbf{V}^{\pm}_1=(\mathbf{S}_1\pm\mathbf{S}_7),\quad \mathbf{V}^{\pm}_2=(\mathbf{S}_3\pm\mathbf{S}_6) , \tag{4.7}$$

we express the energy of the plaquette in the form

$$\begin{aligned} E=&J^{aa}V_1^{+a}V_2^{+a}+J^{bb}V_1^{+b}V_2^{+b}+J^{cc}V_1^{+c}V_2^{+c}\\ &+D^a(V_2^{+c}V_1^{+b}-V_2^{+b}V_1^{+c})\\ &+D^c(V_1^{-a}V_2^{-b}-V_1^{-b}V_2^{-a})\\ &+J^{ac}(V_1^{-a}V_2^{-c}+V_1^{-c}V_2^{-a}) . \end{aligned} \tag{4.8}$$

If the (classical) magnitude of $\mathbf{S}_i$ is $\frac{1}{2}$, then

$$(V_1^+)^2+(V_1^-)^2=(V_2^+)^2+(V_2^-)^2=1 . \tag{4.9}$$

This equation allows us to consider the Hamiltonian (4.8) formally as an exchange Hamiltonian for two six-dimensional unit vectors $\hat{V}_1$ and $\hat{V}_2$, with the direct prod-

uct of the "positive" (p) subspace, containing the vectors $\mathbf{V}_{1,2}^{+}$, and the "negative" (n) subspace, where the components of $\mathbf{V}_{1,2}^{-}$ reside. The 6×6 anisotropy tensor (4.8) does not mix components belonging to these p and n subspaces. Hence we can diagonalize (4.8) by separate orthogonal transformations in the two subspaces. The necessary transformation in the p subspace is a site-dependent rotation around $\hat{a}$, analogous to the one discussed in Ref. 10 [namely, a rotation of $\mathbf{V}_1^+$ by an angle $-\theta$ and a rotation of $\mathbf{V}_2^+$ by an angle θ, where $\tan2\theta=2D^a/(J^{cc}+J^{bb})$]. In the n subspace, the transformation is also a site-dependent rotation. In the new basis, the energy becomes

$$E=J^{+aa}\tilde{V}_1^{+a}\tilde{V}_2^{+a}+J^{+bb}\tilde{V}_1^{+b}V_2^{+b}+J^{+cc}\tilde{V}_1^{+c}\tilde{V}_2^{+c}+J^{-aa}\tilde{V}_1^{-a}\tilde{V}_2^{-a}+J^{-bb}\tilde{V}_1^{-b}\tilde{V}_2^{-b}+J^{-cc}\tilde{V}_1^{-c}\tilde{V}_2^{-c}\ , \tag{4.10a}$$

where the diagonal exchange tensor $\overleftrightarrow{J}$ is given by

$$\begin{aligned} &J^{+aa}=J^{+bb}=J^{aa}=J+A_{kl}^{xy}=J+\frac{(D^a)^2-(D^c)^2}{4J}\ , \\ &J^{+cc}=J-A_{kl}^{zz}=J+|\mathbf{D}|^2/4J\ , \\ &J^{-aa}=J^{-bb}=D^c\sqrt{1+(D^a)^2/4J^2},\quad J^{-cc}=0\ . \end{aligned} \tag{4.10b}$$

Note that J^{+cc} is *always* the largest eigenvalue. Thus, with the exception of the special cases of accidental degeneracy (with two or more identical largest eigenvalues) the antiferromagnetic order-parameter vector of the classical ground-state configuration of orthorhombic La_2CuO_4 is directed along the orthorhombic $\hat{c}$ axis. Note that this is not a quantitative result. In order to obtain it, it is sufficient to consider the symmetry of the lattice, taking into account the hidden symmetry of the one-bond superexchange interactions, *without any need to calculate and compare* various anisotropy parameters.

Clearly, when $D^c\ll J$ the ground-state configuration and the low-energy excitations can be described in terms of the p-subspace coordinates only. Indeed, to excite the "negative" degrees of freedom, one needs to overcome a gap of order J, while the gap for the low-energy spin-wave excitations (confined to the p subspace) is of order $D^c\ll J$ [see Eq. (4.10b)].

We therefore conclude that $\mathbf{V}_1^-=\mathbf{V}_2^-=0$, and therefore $\mathbf{S}_1=\mathbf{S}_7$ and $\mathbf{S}_3=\mathbf{S}_6$ (see Fig. 1). We thus arrive at the situation with two sublattices,

$$\mathbf{M}_1=\mathbf{S}_1=\mathbf{S}_7,\quad \mathbf{M}_2=\mathbf{S}_3=\mathbf{S}_6\ . \tag{4.11}$$

Clearly, translations of the plaquette with the spins constrained by Eq. (4.11) are not frustrated and such a plaquette indeed represents the magnetic elementary cell. The corresponding thermodynamic potential is naturally written in terms of two sublattice magnetizations [cf. Eqs.(1.2) and (3.2)],

$$F=J^{aa}M_1^aM_2^a+J^{bb}M_1^bM_2^b+J^{cc}M_1^cM_2^c+D^a(M_2^cM_1^b-M_2^bM_1^c)\ . \tag{4.12}$$

It follows from Eq. (4.12), that the Dzyaloshinsky vector [see Eq.(1.2)] is identified *microscopically* by the projection of the Moriya vector $\mathbf{D}_{kl}$ onto the orthorhombic $\hat{a}$ axis. This explains the agreement between the experiments and calculations[3,4] based in fact on Eq. (4.12), when J^{bc} of Refs. 3 and 4 is interpreted as $|D^a|$ rather than $|\mathbf{D}|$.

V. CONTRIBUTION FROM DIRECT EXCHANGE

So far we have concentrated solely on the (antiferromagnetic) superexchange[13] interaction which is believed (see, e.g., Refs. 6 and 13) to dominate the exchange in antiferromagnetic insulators. On the level of the electron Hamiltonian, this assumption means that the Hubbard on-site energy U is the only relevant electron-electron correlation parameter. The exchange part of the two-site Coulomb correlations, neglected in the Hamiltonian (2.1), gives rise to the direct exchange[13] interaction, which is always ferromagnetic (see Ref. 13). Let us stress that even though the *isotropic* part of the spin Hamiltonian is determined by superexchange, the direct exchange contribution to the *anisotropy* parameters may still be qualitatively important, especially in the cases when frustration does not completely wipe out the hidden symmetry of the one-bond superexchange interaction. Specifically, it follows from Eq. (4.10b) that the in-plane and out-of-plane gaps of the spin-wave spectra are *equal* to one another. The origin of this hard-plane symmetry is easy to understand. It follows from Eq. (3.2) that the (superexchange) O(3) symmetry of F^+ is broken by an *easy axis* anisotropy of F^-. Clearly the O(2) symmetry is left untouched by the frustration and is manifested in the abovementioned equality of the gaps.

This is in contrast to the experimental fact (see Ref. 3) that the out-of-plane gap is twice larger than the in-plane one. One possible source of this breakdown of the hard-plane symmetry may involve the direct exchange contribution to the anisotropy tensor. In Appendix C we show that the leading-order direct exchange anisotropy is symmetric,with an (antiferromagnetic) easy plane which is indeed parallel to the copper oxide plane. This may account for the fact that the out-of-plane gap is the largest one. Taking into account the direct exchange contribution, one ends up with the spin Hamiltonian which is identical to the phenomenological Hamiltonian of Refs. 3 and 4.

VI. CONCLUSIONS

(1) We presented a derivation of the macroscopic spin Hamiltonian describing the CuO_2 planes of La_2CuO_4, based on nearest-neighbor superexchange interactions. The importance of including the symmetric superexchange anisotropies was demonstrated. The assumption that the antisymmetric anisotropy represents the leading-order anisotropy is unjustified, and may yield incorrect results.

(2) We have shown that if the superexchange anisotropy is bond independent, then it *does not lift* the degeneracy of the ground state of the spin system. The weak ferromagnetism of the orthorhombic La_2CuO_4 can be explained on the basis of the theory of superexchange interactions *only* due to the nontrivial bond dependence of

the one-bond Moriya vectors $\mathbf{D}_{kl}$ and the symmetric anisotropy tensors $\overleftrightarrow{A}_{kl}$.

(3) Considering only the superexchange terms, our approach predicts the absence of weak ferromagnetism in the classical ground-state spin configuration of the low-temperature tetragonal phase.

(4) We showed that the single-plane superexchange interaction alone cannot account for the experimentally measured difference in magnitudes of the spin-wave in-plane and out-of-plane gaps. The leading-order direct exchange contribution to the anisotropy, which is of an easy-plane type, may explain this difference.

(5) The resulting macroscopic mean-field Hamiltonian is identical to the one used phenomenologically by Thio *et al.*[4] to account for the observable magnetic properties of La_2CuO_4.

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APPENDIX A: SYMMETRY PROPERTIES OF $\hat{t}$ AND $\mathbf{t}$

Referring to Fig. 1, we denote by $\phi^d_{1,3}$ the orbitals on the 1 and 3 copper ions and by $\phi^p_{2,4,5}$ the orbitals on the 2, 4, and 5 oxygen ions. We also denote by $\mathbf{L}$ the angular momentum operator. The lattice potential is invariant under the following three transformations: (a) rotation by π around an axis perpendicular to the CuO_2 plane and containing an oxygen ion; (b) refections in the plane perpendicular to the $\hat{a}$ axis and containing a Cu ion; (c) inversion about a center located on a copper ion. Under these symmetry transformations,

$$\hat{t}_{ki}\sim\phi_k\phi_i,\quad \mathbf{t}_{ki}\sim\phi_k\mathbf{L}\phi_i\ , \tag{A1}$$

where $\alpha\sim\beta$ means that α transforms like β and $\hat{t}$ and $\mathbf{t}$ are defined in Eqs. (2.5)–(2.7).

Let us now analyze the relations among the various $\mathbf{t}$'s resulting from the three transformations.

(a) Under this transformation (where the coordinate origin is located on an oxygen ion)

$$\begin{aligned}&\phi^p_2\rightarrow-\phi^p_2,\quad \phi^d_{1,3}\rightarrow\phi^d_{3,1}\ ,\\ &L^{x,y}\rightarrow-L^{x,y},\quad L^z\rightarrow L^z\ .\end{aligned} \tag{A2}$$

The first two relations hold due to the nondegeneracy of the $2p_{x,y}$ oxygen levels and $3d_{x^2-y^2}$ copper levels in the orthorhombic phase. From Eqs. (A1) and (A2) we find

$$\begin{aligned}&\hat{t}_{12}=-\hat{t}_{32}=\hat{t}\ ,\\ &t^{x,y}_{12}=t^{x,y}_{32}=t^{x,y}\ ,\\ &t^z_{12}=-t^z_{32}=t^z\ .\end{aligned} \tag{A3}$$

(b) Under this transformation (where the coordinate origin is on the 1 Cu ion)

$$\begin{aligned}&\phi^p_2\rightarrow-\phi^p_5,\quad \phi^d_1\rightarrow-\phi^d_1\ ,\\ &L^{x,y}\rightarrow L^{y,x},\quad L^z\rightarrow-L^z\ .\end{aligned} \tag{A4}$$

Hence

$$\hat{t}_{12}=\hat{t}_{15},\quad t^{x,y}_{12}=t^{y,x}_{15},\quad t^z_{12}=-t^z_{15}\ . \tag{A5}$$

(c) Under this transformation (where the coordinate origin in on the 3 Cu ion)

$$\phi^p_2\rightarrow-\phi^p_4,\quad \phi^d_3\rightarrow\phi^d_3,\quad L^{x,y,z}\rightarrow L^{x,y,z}\ . \tag{A6}$$

Hence we find

$$\hat{t}_{32}=-\hat{t}_{34},\quad \mathbf{t}_{32}=-\mathbf{t}_{34}\ . \tag{A7}$$

From Eqs. (A.3) and (A.7) it follows that

$$\hat{t}_{12}=\hat{t}_{34},\quad t^{x,y}_{12}=-t^{x,y}_{34},\quad t^z_{12}=t^z_{34}\ . \tag{A8}$$

Clearly, upon inverting the sign of the distortion angle θ [i.e., the O(2)–O(5) row of oxygens goes down and the row containing O(4) moves up] the new $\hat{t}_{12}$ and $\mathbf{t}_{12}$ must be identical to the old $\hat{t}_{34}$ and $\mathbf{t}_{34}$, and vice versa. This yields, according to Eq. (A8) that $\hat{t}$ and t^z are even in the distortion angle θ (leading to the orthorhombic phase), while t^x and t^y are odd. Clearly, t^z emerges only to second order in θ (while $\hat{t}$ is nonzero even in the undistorted lattice). Indeed, when $\theta=0$ the lattice is invariant under reflections in the planes containing the particular bond and parallel and perpendicular to the CuO_2 plane. It is easy to show that a nonzero $\mathbf{t}_{ki}$ violates these additional symmetries (while a nonzero $\hat{t}$ is still allowed). Thus to leading order, $\hat{t}\sim\theta^0$, $t^{x,y}\sim\theta$ (see also Ref. 9), and $t^z\sim\theta^2$. It follows from Eqs. (2.13) and (2.17) that to first order in θ the vectors $\mathbf{D}_{kl}$ and $\mathbf{t}_{ki}$ are parallel to one another.

APPENDIX B: THE RELATIVE MAGNITUDE OF THE COMPONENTS OF $\mathbf{t}_{ki}$

In this appendix we demonstrate that the vector $\tilde{t}_{ki}=(t^x_{ki},t^y_{ki},0)$ [Eqs. (2.5)–(2.7)] is almost perpendicular to the bond $\langle kl\rangle$. Since to first order in the distortion angle θ Moriya's vector $\mathbf{D}_{kl}$ is parallel to $\tilde{t}_{ki}$ (see Appendix A), it follows that $\mathbf{D}_{kl}$ is almost perpendicular to the bond $\langle kl\rangle$.

To show this, we take as an example the bond $\langle 12\rangle$ in Fig. 1, directed along the $\hat{x}$ axis, and focus on the ratio t^x_{12}/t^y_{12}. In the *undistorted* lattice $\mathbf{t}_{12}$ is zero. In order to estimate the ratio in the *distorted* system to first order in θ, it is sufficient to consider the overlaps of the orbital $|\phi^p_2\rangle$ with the orbitals $\mathbf{L}|\phi^d_1\rangle$. Hence we have

$$\frac{t^x_{12}}{t^y_{12}}\sim\frac{\langle\phi^d_1|L^x|\phi^p_2\rangle}{\langle\phi^d_1|L^y|\phi^p_2\rangle}\ . \tag{B1}$$

In the local coordinate system (x',y',z'), defined by the oxygen octahedron, the $3d_{x^2-y^2}$ orbital $|\phi^d_{b1}\rangle=|x'^2-y'^2\rangle$ is the ground state. The operation of the angular momentum on this state produces the orbital $|y'z'\rangle$ in the case of L^x and $|x'z'\rangle$ in the case of L^y (both

with matrix elements of the same order of magnitude). Expressing these orbitals in the "undistorted" coordinates, it is easy to show that to the first order in the distortion angle their overlaps with the $2p_x$ orbital $|\phi_2^p\rangle = |x-a\rangle$ (where a is a length of the bond) can be estimated as

$$\langle \phi_1^d | L^x | \phi_2^p \rangle \sim \langle y^2 - z^2 | x-a \rangle$$
$$\langle \phi_1^d | L^y | \phi_2^p \rangle \sim \langle z^2 - x^2 | x-a \rangle \ . \tag{B2}$$

It is clear that the overlap of $|x^2\rangle$ with $|x-a\rangle$ dominates in Eq. (B2), leading to the conclusion that $t_{12}^y \gg t_{12}^x$.

APPENDIX C: THE PRINCIPAL AXES OF THE DIRECT EXCHANGE ANISOTROPY TENSOR

In this appendix we show that the leading-order direct exchange contribution to the spin Hamiltonian is an easy-plane anisotropy.

In order to account for the direct (or "potential," see Ref. 15) exchange interactions in the meaning introduced by Anderson,[13] one has to append the Hubbard Hamiltonian (2.1) with terms describing the Coulomb interaction of the holes occupying neighboring copper and oxygen ions and then to repeat the calculations of Sec. II. Below, however, we avoid the necessity to eliminate the oxygen degrees of freedom by considering the simpler problem of the "pre-Anderson" direct exchange, resulting from the Coulomb interaction of the holes occupying two neighboring copper ions. We are allowed to do so because we are concerned here not with the magnitudes of the different eigenvalues of the direct exchange anisotropy tensor but rather with their ratios. It will be clear from the following that these ratios do not depend on details of the relevant orbitals and are determined, in fact, only by their *symmetry* properties, which are the same for the otherwise two different situations.

Consider the bond connecting the two copper ions 1 and 3 of Fig. 1. To leading order, the symmetric part of the direct exchange anisotropy contribution to the bond exchange energy is given by[16]

$$H_{13}^d = -2\lambda^2 \sum_m \frac{J(m0)}{(\epsilon_m - \epsilon_0)^2} \mathbf{S}_1 \cdot [2\mathbf{L}_{m0}\mathbf{L}_{m0}^* - (\mathbf{L}_{m0}\cdot\mathbf{L}_{m0}^*)\cdot\overleftrightarrow{I}]\cdot\mathbf{S}_3 \ . \tag{C1}$$

Here m and 0 label, respectively, the excited crystal levels and the ground state of the hole on the Cu ion, λ is the strength of the spin-orbit coupling, $\mathbf{L}_{m0}$ are the matrix elements of the angular momentum and

$$J(m0) = \int\int \phi_{1m}^*(\mathbf{r}_1)\phi_{30}^*(\mathbf{r}_3)\frac{e^2}{r_{13}}\phi_{1m}(\mathbf{r}_3) \times \phi_{30}(\mathbf{r}_1)d\mathbf{r}_1 d\mathbf{r}_3 \ . \tag{C2}$$

It is easy to check that $J(m0)$ has nonzero components even in the undistorted (i.e., high-temperature tetragonal) phase. Clearly, this "tetragonal" contribution, which is $\sim\theta^0$, represents the leading-order contribution to the direct exchange anisotropy. Note also that $\mathbf{L}_{mo}\|\hat{x}$ for transition to the ϕ_{yz} orbital, $\mathbf{L}_{mo}\|\hat{y}$ for transition to the ϕ_{xz} orbital, and $\mathbf{L}_{mo}\|\hat{z}$ for transition to the ϕ_{xy} orbital. In the tetragonal phase the ϕ_{yz} and ϕ_{xz} orbitals are degenerate and their energy (for holes) is higher than that of ϕ_{xy}. Next, in order to compare the various $J(m0)$ note [see Eq. (C2)] that $J(m0)$ is proportional to the square of the overlap of ϕ_{1m} and ϕ_{30}. Thus we conclude that for the bond along the $\hat{x}$ direction

$$J(xy) = J(xz) > J(yz) \ , \tag{C3a}$$

and

$$\epsilon_{xy} < \epsilon_{xz} = \epsilon_{yz} \ . \tag{C3b}$$

Collecting these observations we may rewrite Eq. (C1) in the form

$$H_{13}^d = -\mathbf{S}_1\cdot\{K_1\hat{x}\hat{x} + K_2\hat{y}\hat{y} + K_z\hat{z}\hat{z}\}\cdot\mathbf{S}_3 \ , \tag{C4}$$

where $K_z > K_2 > K_1 > 0$. For the bond along the $\hat{y}$ direction we have to replace K_1 by K_2 and vice versa. Assuming now that we have only two sublattices and summing over all the one-bond expressions we obtain for the direct exchange contribution to the free energy

$$F^d = -J^d\mathbf{M}_1\cdot\mathbf{M}_2 + [K_z - (K_1+K_2)/2](M_1^x M_2^x + M_1^y M_2^y) \ , \tag{C5}$$

which represents an easy-plane antiferromagnet.

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