Dzyaloshinsky-Moriya antisymmetric exchange coupling in cuprates: Oxygen effects

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We revisit a problem of Dzyaloshinsky-Moriya antisymmetric exchange coupling for a single bond in cuprates specifying the local spin-orbital contributions to Dzyaloshinsky vector focusing on the oxygen term. The Dzyaloshinsky vector and respective weak ferromagnetic moment is shown to be a superposition of comparable and, sometimes, competing local Cu and O contributions. The intermediate oxygen ^{17}O Knight shift is shown to be an effective tool to inspect the effects of Dzyaloshinsky-Moriya coupling in an external magnetic field. We predict the effect of *strong* oxygen weak antiferromagnetism in edge-shared CuO_2 chains due to uncompensated oxygen Dzyaloshinsky vectors. Finally, we revisit the effects of symmetric spin anisotropy, in particular, those directly induced by Dzyaloshinsky-Moriya coupling.

I. INTRODUCTION

Fifthy years ago Borovik-Romanov and Orlova[1] have discovered the phenomenon of weak ferromagnetism which origin was shortly after[2] bound up with exchange-relativistic effect mainly with antisymmetric exchange coupling. Starting from pioneer papers by Dzyaloshinsky[2] and Moriya[3] the Dzyaloshinsky-Moriya (DM) antisymmetric exchange coupling was extensively investigated in 60-80ths in connection with weak ferromagnetism focusing on hematite α-Fe_2O_3 and orthoferrites $RFeO_3$.[4] The stimulus to a renewed interest to the subject was given by the cuprate problem, in particular, by the weak ferromagnetism observed in La_2CuO_4[5] and many other interesting effects for the DM systems, in particular, the "field-induced gap" phenomena.[6] At variance with typical 3D systems such as orthoferrites, cuprates are characterised by a low-dimensionality, large diversity of Cu-O-Cu bonds including corner- and edge-sharing, different ladder configurations, strong quantum effects for $s = 1/2$ Cu^{2+} centers, and a particularly strong Cu-O covalency resulting in a comparable magnitude of hole charge/spin densities on copper and oxygen sites. Several groups (see, e.g., Refs.7,8,9) developed the microscopic model approach by Moriya for different 1D and 2D cuprates, making use of different perturbation schemes, different types of low-symmetry crystalline field, different approaches to intra-atomic electron-electron repulsion. However, despite a rather large number of publications and hot debates (see, e.g., Ref.10) the problem of exchange-relativistic effects, that is of antisymmetric exchange and related problem of spin anisotropy in cuprates remains to be open (see, e.g., Refs.11,12 for recent experimental data and discussion). Common shortcomings of current approaches to DM coupling in 3d oxides concern a problem of allocation of Dzyaloshinsky vector and respective "weak" (anti)ferromagnetic moments, and full neglect of spin-orbital effects for "nonmagnetic" oxygen O^{2-} ions, which are usually believed to play only indirect intervening role. From the other hand, the oxygen ^{17}O NMR-NQR studies of weak ferromagnet La_2CuO_4[13] seem to evidence unconventional local oxygen "weak-ferromagnetic" polarization which origin cannot be explained in frames of current models. All this stimulated the critical revisit of many old approaches to the spin-orbital effects in 3d oxides, starting from the choice of proper perturbation scheme and effective spin Hamiltonian model, implied usually only indirect intervening role played by "nonmagnetic" oxygen O^{2-} ions.

In this paper we revisit a problem of DM antisymmetric exchange coupling for a single bond in cuprates specifying the local spin-orbital contributions to Dzyaloshinsky vector focusing on the oxygen term. In Sec.II we present a short overview of the spin-Hamiltonian of a typical three-center (Cu-O-Cu) two-hole system. Microscopic theory of DM coupling is presented in Sec.III. The Dzyaloshinsky vector is shown to be a superposition of comparable and, sometimes, competing local Cu and O contributions. In Sec.IV we examine a response of DM coupled Cu_1-O-Cu_2 bond on an uniform and staggered external fields, and demonstrate some unusual manifestations of local oxygen contribution to DM coupling. The intermediate oxygen ^{17}O Knight shift is shown to be an effective tool to inspect the effects of DM coupling in an external magnetic field. In Sec.V we revisit a problem of symmetric spin anisotropy with inclusion of local oxygen spin-orbital contributions.

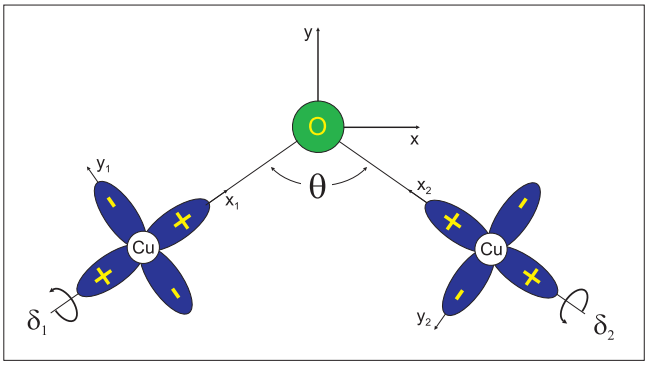

FIG. 1: Geometry of the three-center (Cu-O-Cu) two-hole system with ground Cu $3d_{x^2-y^2}$ states.

II. SPIN-HAMILTONIAN

For illustration, below we address a typical for cuprates the three-center (Cu_1-O-Cu_2) two-hole system with tetragonal Cu on-site symmetry and ground Cu $3d_{x^2-y^2}$ states (see Fig. 1) which conventional bilinear spin Hamiltonian is written in terms of copper spins as follows

$$\hat{H}_s(12) = J_{12}(\hat{\mathbf{s}}_1 \cdot \hat{\mathbf{s}}_2) + \mathbf{D}_{12} \cdot [\hat{\mathbf{s}}_1 \times \hat{\mathbf{s}}_2] + \hat{\mathbf{s}}_1 \overleftrightarrow{\mathbf{K}}_{12} \hat{\mathbf{s}}_2 \,, \quad (1)$$

where $J_{12} > 0$ is an exchange integral, $\mathbf{D}_{12}$ is the Dzyaloshinsky vector, $\overleftrightarrow{\mathbf{K}}_{12}$ is a symmetric second-rank tensor of the anisotropy constants. In contrast with $J_{12}, \overleftrightarrow{\mathbf{K}}_{12}$, the Dzyaloshinsky vector $\mathbf{D}_{12}$ is antisymmetric with regard to the site permutation: $\mathbf{D}_{12} = -\mathbf{D}_{21}$. Hereafter we will denote $J_{12} = J, \overleftrightarrow{\mathbf{K}}_{12} = \overleftrightarrow{\mathbf{K}}, \mathbf{D}_{12} = \mathbf{D}$, respectively. It should be noted that making use of effective spin Hamiltonian (1) implies a removal of orbital degree of freedom that calls for a caution with DM coupling as it changes both a spin multiplicity, and an orbital state.

It is clear that the applicability of such an operator as $\hat{H}_s(12)$ to describe all the "oxygen" effects is extremely limited. Moreover, the question arises in what concerns the composite structure and spatial distribution of what that be termed as the Dzyaloshinsky vector density. Usually this vector is assumed to be located on the bond connecting spins 1 and 2.

Strictly speaking, spin Hamiltonian $H_s(12)$ can be viewed as a result of the projection onto the purely ionic $Cu_1^{2+}(3d_{x^2-y^2})$-$O^{2-}(2p^6)$-$Cu_2^{2+}(3d_{x^2-y^2})$ ground state of the two-hole spin Hamiltonian

$$\hat{H}_s = \sum_{i<j} I(i,j)(\hat{\mathbf{s}}(i) \cdot \hat{\mathbf{s}}(j)) + \sum_{i<j} (\mathbf{d}(i,j) \cdot [\hat{\mathbf{s}}(i) \times \hat{\mathbf{s}}(j)]) + \sum_{i<j} \hat{\mathbf{s}}(i) \overleftrightarrow{\mathbf{K}}(i,j) \hat{\mathbf{s}}(j) \,, \quad (2)$$

which implies not only both copper and oxygen hole location, but allows to account for purely oxygen two-hole configurations. Moreover, such a form allows us to neatly separate both one-center and two-center effects. Two-hole spin Hamiltonian can be projected onto three-center states incorporating the Cu-O charge transfer effects.

For a composite two $s = 1/2$ spins system one should consider three types of the vector order parameters:

$$\hat{\mathbf{S}} = \hat{\mathbf{s}}_1 + \hat{\mathbf{s}}_2; \; \hat{\mathbf{V}} = \hat{\mathbf{s}}_1 - \hat{\mathbf{s}}_2; \; \hat{\mathbf{T}} = 2[\hat{\mathbf{s}}_1 \times \hat{\mathbf{s}}_2] \quad (3)$$

with a kinematic constraint:

$$\hat{\mathbf{S}}^2 + \hat{\mathbf{V}}^2 = 3\hat{\mathbf{I}}; \; (\hat{\mathbf{S}} \cdot \hat{\mathbf{V}}) = 0; \; (\hat{\mathbf{T}} \cdot \hat{\mathbf{V}}) = 6i; \; [\hat{\mathbf{T}} \times \hat{\mathbf{V}}] = \hat{\mathbf{S}}. \quad (4)$$

In a sense the $\hat{\mathbf{V}}$ operator describes the effect of local antiferromagnetic order, while $\hat{\mathbf{T}}$ operator may be associated with a vector chirality.[14] In recent years, phases with broken vector chirality in frustrated quantum spin chains have attracted considerable interest. Such phases are characterized by nonzero long-range correlations of the vector order parameter $\langle \hat{\mathbf{T}} \rangle$. Interestingly that a chirally ordered phase can manifest itself as a "nonmagnetic" one, with $\langle \hat{\mathbf{S}} \rangle = \langle \hat{\mathbf{V}} \rangle = 0$.

Both $\hat{\mathbf{T}}$ and $\hat{\mathbf{V}}$ operators change the spin multiplicity with matrix elements

$$\langle 00|\hat{T}_m|1n\rangle = -\langle 1n|\hat{T}_m|00\rangle = i\delta_{mn};$$

$$\langle 00|\hat{V}_m|1n\rangle = \langle 1n|\hat{V}_m|00\rangle = \delta_{mn}, \quad (5)$$

where we made use of Cartesian basis for $S = 1$. The eigenstates of the operators $\hat{V}_n$ and $\hat{T}_n$ with nonzero eigenvalues ± 1 form Néel doublets $\frac{1}{\sqrt{2}}(|00\rangle \pm |1n\rangle)$ and DM doublets $\frac{1}{\sqrt{2}}(|00\rangle \pm i|1n\rangle)$, respectively. The Néel doublets correspond to classical collinear antiferromagnetic spin configurations, while the DM doublets correspond to quantum spin configurations which sometimes are associated with a rectangular 90^0 spin ordering in the plane orthogonal to the Dzyaloshinsky vector.

It should be noted that the both above spin Hamiltonians can be reduced to within a constant to a spin operator acting in a total spin space

$$\hat{H}_S = \frac{1}{4} J(\hat{\mathbf{S}}^2 - \hat{\mathbf{V}}^2) + \frac{1}{2}(\mathbf{D} \cdot \hat{\mathbf{T}}) + \frac{1}{4} \hat{\mathbf{S}} \overleftrightarrow{\mathbf{K}}^S \hat{\mathbf{S}} - \frac{1}{4} \hat{\mathbf{V}} \overleftrightarrow{\mathbf{K}}^V \hat{\mathbf{V}} \,. \quad (6)$$

For simple dipole-like two-ion anisotropy as in Exp. (1) $\overleftrightarrow{\mathbf{K}}^S = \overleftrightarrow{\mathbf{K}}^V = \overleftrightarrow{\mathbf{K}}$, though in general these tensorial parameters can differ from each other. Making use of the anticommutator relations

$$\{\hat{S}_i, \hat{S}_j\} + \{\hat{V}_i, \hat{V}_j\} = 2\delta_{ij}; \; \{\hat{V}_i, \hat{V}_j\} = \{\hat{T}_i, \hat{T}_j\}, \quad (7)$$

we conclude that the effective operator of symmetric anisotropy can be equivalently expressed in terms of symmetric products $\{\hat{S}_i, \hat{S}_j\}$, $\{\hat{V}_i, \hat{V}_j\}$, or $\{\hat{T}_i, \hat{T}_j\}$.

The most general form of the spin Hamiltonian (6) does not discriminate against copper or oxygen contribution and can be used to properly account for oxygen effects. As we will see below the $\mathbf{D}$ and $\overleftrightarrow{\mathbf{K}}$ parameters allow the correct separation of local copper and oxygen contributions.

It should be noted that the total spin representation and overall quantum approach is especially efficient to describe antisymmetric exchange in Cu-Cu dimer systems

(see, e.g. Ref.15 and references therein). Classical approach to $s = 1/2$ spin-Hamiltonian should be applied with a caution, particularly for 1D systems.

Before going to microscopic analysis we should note that the interaction of our three-center system with external spins and/or fields $\hat{H}_{ext}$ is usually addressed by introducing only two types of effective external fields: the conventional Zeeman-like uniform field and unconventional Néel-like staggered field, so that $\hat{H}_{ext}$ reads as follows

$$\hat{H}_{ext} = -(\mathbf{h}^S \cdot \hat{\mathbf{S}}) - (\mathbf{h}^V \cdot \hat{\mathbf{V}}). \quad (8)$$

It should be noted that an ideal Néel state is attainable only in the limit of infinitely large staggered field, therefore for a finite staggered field $\mathbf{h}^V \parallel \mathbf{n}$ the ground state is a superposition of a spin singlet and a Néel state,

$$\Psi = \cos\alpha|00\rangle + \sin\alpha|1n\rangle,\ \tan 2\alpha = \frac{2h^V}{J},$$

which composition reflects the role of quantum effects. For instance, in a Heisenberg spin 1/2 chain with nn exchange the maximal value of staggered field $h^V = J/2$ hence the Ψ function strongly differs from that of Néel state ($\langle\hat{V}_n\rangle = \sin 2\alpha = \frac{1}{\sqrt{2}}$), and quantum mechanical average for a single spin $\langle s_z\rangle \leq \frac{1}{2}\sin\pi/4 = \frac{1}{\sqrt{2}}\cdot\frac{1}{2} \approx 0.71\cdot\frac{1}{2}$ deviates strongly from classical value $\frac{1}{2}$. It should be noted that for the isolated antiferromagnetically coupled spin pair the zero-temperature uniform spin susceptibility turns into zero: $\chi^S = 0$, while for the staggered spin susceptibility we obtain $\chi^V = 2/J$.

III. MICROSCOPIC THEORY OF DM COUPLING IN CUPRATES

A. Preliminaries

For the microscopic expression for Dzyaloshinsky vector to derive Moriya[3] made use of the Anderson's formalism of superexchange interaction[16] with two main contributions of so called kinetic and potential exchange, respectively. Then he took into account the spin-orbital corrections to the effective d-d transfer integral and potential exchange. Such an approach seems to be improper to account for purely oxygen effects. In later papers (see, e.g. Refs.8,17) the authors made use of the Moriya scheme to account for spin-orbital corrections to p-d transfer integral, however, without any analysis of oxygen contribution. It is worth noting that in both instances the spin-orbital renormalization of a single hole transfer integral leads immediately to a lot of problems with correct responsiveness of the on-site Coulomb hole-hole correlation effects. Anyway the effective DM spin-Hamiltonian evolves from the high-order perturbation effects that makes its analysis rather involved and leads to many misleading conclusions.

At variance with the Moriya approach we start with the construction of spin-singlet and spin-triplet wave functions for our three-center two-hole system taking account of the p-d hopping, on-site hole-hole repulsion, and crystal field effects for excited configurations $\{n\}$ (011, 110, 020, 200, 002) with different hole occupation of Cu_1, O, and Cu_2 sites, respectively. The p-d hopping for Cu-O bond implies a conventional Hamiltonian

$$\hat{H}_{pd} = \sum_{\alpha\beta} t_{p\alpha d\beta}\hat{p}^\dagger_\alpha \hat{d}_\beta + h.c.\,, \quad (9)$$

where $\hat{p}^\dagger_\alpha$ creates a hole in the α state on the oxygen site, while $\hat{d}_\beta$ annihilates a hole in the β state on the copper site; $t_{p\alpha d\beta}$ is a pd-transfer integral ($t_{p_x d_{x^2-y^2}} = \frac{\sqrt{3}}{2}t_{p_z d_{z^2}} = t_{pd\sigma} > 0, t_{p_y d_{xy}} = t_{pd\pi} > 0$).

For basic 101 configuration with two $d_{x^2-y^2}$ holes localized on its parent sites we arrive at a perturbed wave function as follows

$$\Psi_{101;SM} = \Phi_{101;SM} + \sum_{\{n\}\Gamma} c_{\{n\}}(^{2S+1}\Gamma)\Phi_{\{n\};\Gamma SM}, \quad (10)$$

where the summation runs both on different configurations and different orbital Γ states. It is worth noting that the probability amplitudes $c_{\{011\}}, c_{\{110\}} \propto t_{pd}, c_{\{200\}}, c_{\{020\}}, c_{\{002\}} \propto t^2_{pd}$. To account for orbital effects for $Cu_{1,2}$ 3d holes and the covalency induced mixing of different orbital states for 101 configuration we should introduce an effective exchange Hamiltonian

$$\hat{H}_{ex} = \frac{1}{2}\sum_{\alpha\beta\gamma\delta\mu\mu'} J(\alpha\beta\gamma\delta)\hat{d}^\dagger_{1\alpha\mu}\hat{d}^\dagger_{2\beta\mu'}\hat{d}_{2\gamma\mu}\hat{d}_{1\delta\mu'} + h.c. \quad (11)$$

Here $\hat{d}^\dagger_{1\alpha\mu}$ creates a hole in the αth 3d orbital on Cu_1 site with spin projection μ. Exchange Hamiltonian (11) involves both spinless and spin-dependent terms, however, it preserves the spin multiplicity of Cu_1-O-Cu_2 system. Exchange parameters $J(\alpha\beta\gamma\delta)$ are of the order of t^4_{pd}.

Then we introduce a standard effective spin Hamiltonian operating in a fourfold spin-degenerated space of basic 101 configuration with two $d_{x^2-y^2}$ holes and can straightforwardly calculate the singlet-triplet separation to find effective exchange integral $J_{12} = J(d_{x^2-y^2}d_{x^2-y^2}, d_{x^2-y^2}d_{x^2-y^2})$, calculate the singlet-triplet mixing due to three *local* spin-orbital terms, $V_{so}(Cu_1), V_{so}(O), V_{so}(Cu_2)$, respectively, to find the *local* contributions to Dzyaloshinsky vector:

$$\mathbf{D} = \mathbf{D}^{(1)} + \mathbf{D}^{(0)} + \mathbf{D}^{(2)}. \quad (12)$$

Local spin-orbital coupling is taken as follows:

$$V_{so} = \sum_i \xi_{nl}(\mathbf{l}_i \cdot \mathbf{s}_i) = \frac{\xi_{nl}}{2}[(\hat{\mathbf{l}}_1 + \hat{\mathbf{l}}_2)\cdot\hat{\mathbf{S}} + (\hat{\mathbf{l}}_1 - \hat{\mathbf{l}}_2)\cdot\hat{\mathbf{V}}]$$

$$= \hat{\mathbf{\Lambda}}^S \cdot \hat{\mathbf{S}} + \hat{\mathbf{\Lambda}}^V \cdot \hat{\mathbf{V}} \quad (13)$$

with a single particle constant $\xi_{nl} > 0$ for electrons and $\xi_{nl} < 0$ for holes. We make use of orbital matrix elements: for Cu 3d holes $\langle d_{x^2-y^2}|l_x|d_{yz}\rangle = \langle d_{x^2-y^2}|l_y|d_{xz}\rangle = i, \langle d_{x^2-y^2}|l_z|d_{xy}\rangle = -2i$, $\langle i|l_j|k\rangle = -i\epsilon_{ijk}$ with Cu $3d_{yz}$=$|1\rangle$, $3d_{xz}$=$|2\rangle$ $3d_{xy}$=$|3\rangle$, and for O 2p holes $\langle p_i|l_j|p_k\rangle = i\epsilon_{ijk}$. Free cuprous Cu^{2+} ion is described by a large spin-orbital coupling with $|\xi_{3d}| \cong 0.1$ eV (see, e.g., Ref.18), though its value may be significantly reduced in oxides. Information regarding the ξ_{2p} value for the oxygen O^{2-} ion in oxides is scant if any. Usually one considers the spin-orbital coupling on the oxygen to be much smaller than that on the copper, and therefore may be neglected.[19,20] However, even for a free oxygen atom the electron spin orbital coupling turns out to reach of appreciable magnitude: $\xi_{2p} \cong 0.02$ eV,[21] while for the oxygen O^{2-} ion in oxides one expects the visible enhancement of spin-orbital coupling due to a larger compactness of 2p wave function.[22] If to account for $\xi_{nl} \propto \langle r^{-3}\rangle_{nl}$ and compare these quantities for the copper ($\langle r^{-3}\rangle_{3d} \approx 6-8$ a.u.[22]) and the oxygen ($\langle r^{-3}\rangle_{2p} \approx 4$ a.u.[13,22]) we arrive at a maximum factor two difference in ξ_{3d} and ξ_{2p}.

Hereafter we assume a tetragonal symmetry at Cu sites with local coordinate systems as shown in Fig.1. The global xyz coordinate system is chosen so as Cu_1-O-Cu_2 plane coincides with xy-plane, x-axis is directed along Cu_1-Cu_2 bond (see Fig.1). In such a case the basic unit vectors $\mathbf{x}, \mathbf{y}, \mathbf{z}$ can be written in local systems of Cu_1 and Cu_2 sites as follows:

$$\mathbf{x} = (\sin\frac{\theta}{2}, -\cos\frac{\theta}{2}\cos\delta_1, -\cos\frac{\theta}{2}\sin\delta_1);$$

$$\mathbf{y} = (\cos\frac{\theta}{2}, \sin\frac{\theta}{2}\cos\delta_1, \sin\frac{\theta}{2}\sin\delta_1); \mathbf{z} = (0, \sin\delta_1, \cos\delta_1)$$

for Cu_1, while for Cu_2 site θ, δ_1 should be replaced by $-\theta, \delta_2$, respectively.

The exchange integral can be written as follows:

$$J = \sum_{\{n\},\Gamma} [|c_{\{n\}}(^3\Gamma)|^2 E_{^3\Gamma}(\{n\}) - |c_{\{n\}}(^1\Gamma)|^2 E_{^1\Gamma}(\{n\})]. \tag{14}$$

As concerns the DM interaction we deal with two competing contributions. The first is derived as a first order contribution which does not take account of $Cu_{1,2}$ 3d-orbital fluctuations for a ground state 101 configuration. Projecting the spin-orbital coupling (13) onto states (10) we see that $\hat{\mathbf{\Lambda}}^V \cdot \hat{\mathbf{V}}$ term is equivalent to purely spin DM coupling with local contributions to Dzyaloshinsky vector

$$D_i^{(m)} = -2i\langle 00|V_{so}(m)|1i\rangle = -2i \sum_{\{n\}\Gamma_1,\Gamma_2} c^*_{\{n\}}(^1\Gamma_1) c_{\{n\}}(^3\Gamma_2) \langle \Phi_{\{n\};\Gamma_1 00}|\Lambda_i^V|\Phi_{\{n\};\Gamma_2 1i}\rangle \tag{15}$$

In all the instances the nonzero contribution to the local Dzyaloshinsky vector is determined solely by the spin-orbital singlet-triplet mixing for the on-site 200, 020, 002 and two-site 110, 011 two-hole configurations, respectively. For on-site two-hole configurations we have $\mathbf{D}^{(200)} = \mathbf{D}^{(1)}$, $\mathbf{D}^{(020)} = \mathbf{D}^{(0)}$, $\mathbf{D}^{(002)} = \mathbf{D}^{(2)}$.

The second contribution, associated with $Cu_{1,2}$ 3d-orbital fluctuations within a ground state 101 configuration, is more familiar one and evolves from a second order combined effect of $Cu_{1,2}$ spin-orbital $V_{so}(Cu_{1,2})$ and effective orbitally anisotropic Cu_1-Cu_2 exchange coupling

$$D_i^{(m)} = -2i\langle 00|V_{so}(m)|1i\rangle = -2i \sum_{\Gamma} \frac{\langle\{101\};\Gamma_s 00|\hat{\Lambda}_i^V|\{101\};\Gamma 1i\rangle\langle\{101\};\Gamma 1i|\hat{H}_{ex}|\{101\};\Gamma_t 1i\rangle}{E_{^3\Gamma_t}(\{101\}) - E_{^3\Gamma}(\{101\})}$$
$$-2i \sum_{\Gamma} \frac{\langle\{101\};\Gamma_s 00|\hat{H}_{ex}|\{101\};\Gamma 00\rangle\langle\{101\};\Gamma 00|\hat{\Lambda}_i^V|\{101\};\Gamma_t 1i\rangle}{E_{^1\Gamma_s}(\{101\}) - E_{^1\Gamma}(\{101\})} \tag{16}$$

It should be noted that at variance with the original Moriya approach[3] both spinless and spin-dependent parts of exchange Hamiltonian contribute additively and comparably to DM coupling, if one takes account of the same magnitude and opposite sign of the singlet-singlet and triplet-triplet exchange matrix elements on the one hand and orbital antisymmetry of spin-orbital matrix elements on the other hand.

It is easy to see that the contributions of 002 and 200 configurations to Dzyaloshinsky vector bear a similarity

to the respective second type ($\propto V_{so}H_{ex}$) contributions, however, in the former we deal with spin-orbital coupling for two-hole $Cu_{1,2}$ configurations, while in the latter with that of one-hole $Cu_{1,2}$ configurations.

B. Copper contribution

First we address a relatively simple instance of strong rhombic crystal field for intermediate oxygen ion with the crystal field axes oriented along global coordinate x, y, z-axes, respectively. It is worth noting that in such a case the oxygen O $2p_z$ orbital does not play an active role both in symmetric and antisymmetric (DM) exchange interaction as well as Cu $3d_{yz}$ orbital appears to be inactive in DM interaction due to a zero overlap/transfer with oxygen O 2p orbitals.

For illustration, hereafter we address the first contribution (15) of two-hole on-site 200, 002 $d^2_{x^2-y^2}$, $d_{x^2-y^2}d_{xy}$, and $d_{x^2-y^2}d_{xz}$ configurations, which do covalently mix with ground state configuration. Calculating the singlet-triplet mixing matrix elements in the global coordinate system we find all the components of the local Dzyaloshinsky vectors. The Cu_1 contribution turns out to be nonzero only for 200 configuration, and may be written as a sum of several terms. First we present the contribution of singlet $(d^2_{x^2-y^2})^1A_{1g}$ state:

$$D_x^{(1)} = -2i\langle 00|V_{so}(Cu_1)|1x\rangle = \sqrt{2}\xi_{3d}\, c_{200}({}^1A_{1g})[c_{200}({}^3E_g)\cos\delta_1 - 2c_{200}({}^3A_{2g})\sin\delta_1]\cos\frac{\theta}{2};$$

$$D_y^{(1)} = -2i\langle 00|V_{so}(Cu_1)|1y\rangle = -\sqrt{2}\xi_{3d}\, c_{200}({}^1A_{1g})[c_{200}({}^3E_g)\cos\delta_1 - 2c_{200}({}^3A_{2g})\sin\delta_1]\sin\frac{\theta}{2};$$

$$D_z^{(1)} = -2i\langle 00|V_{so}(Cu_1)|1z\rangle = -\sqrt{2}\xi_{3d}\, c_{200}({}^1A_{1g})[c_{200}({}^3E_g)\sin\delta_1 - 2c_{200}({}^3A_{2g})\cos\delta_1], \quad (17)$$

where

$$c_{200}({}^1A_{1g}) = -\frac{3}{2\sqrt{2}}t^2_{pd\sigma}\frac{1}{E_{^1A_{1g}}}\left[\frac{\sin^2\frac{\theta}{2}}{\epsilon_x} - \frac{\cos^2\frac{\theta}{2}}{\epsilon_y}\right],$$

$$c_{200}({}^{1,3}A_{2g}) = -\frac{\sqrt{3}}{4}t_{pd\sigma}t_{pd\pi}\frac{1}{E_{^{1,3}A_{2g}}}\left(\frac{1}{\epsilon_x}+\frac{1}{\epsilon_y}\right)\sin\theta\cos\delta_1,$$

$$c_{200}({}^{1,3}E_g) = -\frac{\sqrt{3}}{4}t_{pd\sigma}t_{pd\pi}\frac{1}{E_{^{1,3}E_g}}\left(\frac{1}{\epsilon_x}+\frac{1}{\epsilon_y}\right)\sin\theta\sin\delta_1,$$

are probability amplitudes for singlet $(d^2_{x^2-y^2})^1A_{1g}$ and singlet/triplet $(d_{x^2-y^2}d_{xy})^{1,3}A_{2g}$, $(d_{x^2-y^2}d_{xz})^{1,3}E_g$ 200 configurations in the ground state wave function, respectively. $E_{^1A_{1g}} = A + 4B + 3C$ is the energy of the two-hole copper singlet with $d^2_{x^2-y^2}$ configuration, $E_{^1A_{2g}} = \epsilon_{xy} + A + 4B + 2C$, $E_{^3A_{2g}} = \epsilon_{xy} + A + 4B$, $E_{^1E_g} = \epsilon_{xz} + A + B + 2C$, $E_{^3E_g} = \epsilon_{xz} + A - 5B$ are the energies of the two-hole copper terms with $d_{x^2-y^2}d_{xy}$ and $d_{x^2-y^2}d_{xz}$ configurations, respectively, A, B, and C are Racah parameters. Taking into account that $c_{002}({}^1A_{1g}) = c_{200}({}^1A_{1g})$, $c_{002}({}^3A_{2g}) = c_{200}({}^3A_{2g})$, $c_{002}({}^3E_{2g}) = c_{200}({}^3E_g)$[23] we see that the Cu_2 contribution to the Dzyaloshinsky vector can be obtained from Exps. (17), if θ, δ_1 replace by $-\theta, \delta_2$, respectively. Interestingly to note that $D^{(1,2)}_{x,y} \propto \sin\theta\sin 2\delta_{1,2}$. Both collinear ($\theta = \pi$) and rectangular ($\theta = \pi/2$) superexchange geometries appear to be unfavorable for copper contribution to antisymmetric exchange, though in the latter the result depends strongly on the relation between the energies of oxygen O $2p_x$ and O $2p_y$ orbitals.

Contribution of singlet $(d_{x^2-y^2}d_{xy})^1A_{2g}$ and $(d_{x^2-y^2}d_{xz})^1E_g$ states to the Dzyaloshinsky vector yields

$$d_x^{(1)} = d^{(1)}\sin\frac{\theta}{2},\ d_y^{(1)} = d^{(1)}\cos\frac{\theta}{2},\ d_z^{(1)} = 0,$$

where $d^{(1)} = \xi_{3d}(c_{200}({}^1A_{2g})c_{200}({}^3E_g) - c_{200}({}^1E_g)c_{200}({}^3A_{2g}))$. Here we deal with a vector directed along Cu_1-O bond which modulus $d^{(1)} \propto \sin^2\theta\sin 2\delta_1$ is determined by a partial cancellation of two terms.

It is easy to see that the copper $V_{so}(1)$ contribution to the Dzyaloshinsky vector for two-site 110 and 011 configurations is determined by a dp-exchange.

C. Oxygen contribution

In frames of the same assumption regarding the orientation of rhombic crystal field axes for intermediate oxygen ion the local oxygen contribution to the Dzyaloshinsky vector for one-site 020 configuration appears to be oriented along local O_z axis and may be written as follows

$$D_z^{(0)} = -2i\langle 00|V_{so}(O)|1z\rangle = \sqrt{2}\xi_{2p}\, c_t(p_xp_y)[c(p_x^2)+c(p_y^2)], \quad (18)$$

where $c(p^2) = c_{020}(p^2)$ with

$$c(p_x^2) = -\frac{3}{2\sqrt{2}} t_{pd\sigma}^2 \frac{\sin^2\frac{\theta}{2}}{\epsilon_x E_s(p_x^2)};\; c(p_y^2) = \frac{3}{2\sqrt{2}} t_{pd\sigma}^2 \frac{\cos^2\frac{\theta}{2}}{\epsilon_y E_s(p_y^2)};$$

$$c_t(p_x p_y) = \frac{3}{8} t_{pd\sigma}^2 \left(\frac{1}{\epsilon_x} + \frac{1}{\epsilon_y}\right) \frac{\sin\theta}{E_t(p_x p_y)} \qquad (19)$$

are probability amplitudes for singlet p_x^2, p_y^2 and triplet $p_x p_y$ 020 configurations in the ground state wave function, respectively; $E_s(p_{x,y}^2) = 2\epsilon_{x,y} + F_0 + \frac{4}{25}F_2$, $E_t(p_x p_y) = \epsilon_x + \epsilon_y + F_0 - \frac{1}{5}F_2$ are the energies of the oxygen two-hole singlet (s) and triplet (t) configurations p_x^2, p_y^2 and $p_x p_y$, respectively, F_0 and F_2 are Slater integrals. This vector can be written as follows[24]

$$\mathbf{D}^{(0)} = D_O(\theta)[\mathbf{r}_1 \times \mathbf{r}_2], \qquad (20)$$

where $\mathbf{r}_{1,2}$ are unit radius-vectors along Cu_1-O, Cu_2-O bonds, respectively, and

$$D_O(\theta) = \frac{9\xi_{2p} t_{pd\sigma}^4}{16} \frac{1}{E_t(p_x p_y)} \left(\frac{1}{\epsilon_x} + \frac{1}{\epsilon_y}\right) \left[\frac{\cos^2\frac{\theta}{2}}{\epsilon_x E_s(p_x^2)} - \frac{\sin^2\frac{\theta}{2}}{\epsilon_y E_s(p_y^2)}\right]. \qquad (21)$$

It is worth noting that $\mathbf{D}^{(0)}$ does not depend on the δ_1, δ_2 angles. The $D_O(\theta)$ dependence is expected to be rather smooth without any singularities for collinear and rectangular superexchange geometries.

The local oxygen contribution to the Dzyaloshinsky vector for two-site 110 and 011 configurations appears to be oriented along local O_z axis as well and may be written as follows

$$D_z^{(0)} = -2i\langle 00|V_{so}(O)|1z\rangle = \xi\left([\mathbf{c}_s(dp) \times \mathbf{c}_t(dp)]_z + [\mathbf{c}_s(pd) \times \mathbf{c}_t(pd)]_z\right), \qquad (22)$$

$$c_{s,t}(dp_x) = -\frac{\sqrt{3}}{2} \frac{t_{pd\sigma}}{E_{s,t}(dp_x)} \sin\frac{\theta}{2},\; c_{s,t}(dp_y) = -\frac{\sqrt{3}}{2} \frac{t_{pd\sigma}}{E_{s,t}(dp_y)} \cos\frac{\theta}{2}\;, \qquad (23)$$

where $c_{s,t}(dp) = c_{110}(dp), c_{s,t}(pd) = c_{011}(dp)$ are probability amplitudes for different singlet (c_s) and triplet (c_t) 110 ($d_{x^2-y^2}p_{x,y}$) and 011 ($p_{x,y}d_{x^2-y^2}$) configurations in the ground state wave function, respectively. The energies $E_{s,t}(dp_{x,y})$ are those for singlet and triplet states of $dp_{x,y}$ configurations, respectively: $E_{s,t}(dp_{x,y}) = \epsilon_{x,y} + K_{dpx,y} \pm I_{dpx,y}$, where $K_{dpx,y}$ and $I_{dpx,y}$ are Coulomb and exchange dp-integrals, respectively. It is easy to see that the nonzero contribution to Dzyaloshinsky vector is determined by a direct dp-exchange and may be written similarly to (20) with

$$D_O(\theta) = \frac{3\xi_{2p} t_{pd\sigma}^2}{8} \frac{1}{\epsilon_x \epsilon_y} \left(\frac{I_{dpx}}{\epsilon_x} - \frac{I_{dpy}}{\epsilon_y}\right) \approx \frac{3\xi_{2p} t_{pd\sigma}^2}{8} \frac{1}{\epsilon_x \epsilon_y} \left(\frac{\sin^2\frac{\theta}{2}}{\epsilon_x} - \frac{\cos^2\frac{\theta}{2}}{\epsilon_y}\right) I_{dp\sigma}, \qquad (24)$$

where we take account only of $dp\sigma$ exchange ($I_{dp\sigma} \propto t_{pd\sigma}^2$).

Thus, the total Dzyaloshinsky vector $\mathbf{D}$ is a superposition of three contributions $\mathbf{D} = \mathbf{D}^{(1)} + \mathbf{D}^{(0)} + \mathbf{D}^{(2)}$ attached to the respective sites. In general, all the vectors can be oriented differently. Their magnitudes strongly depend on the Cu_1-O-Cu_2 bond geometry and crystal field effects, however, comparative analysis of Exps. (17) and (21) given estimations for different parameters typical for cuprates[25] ($t_{pd\sigma} \approx 1.5$ eV, $t_{pd\pi} \approx 0.7$ eV, $A = 6.5$ eV, $B = 0.15$ eV, $C = 0.58$ eV, $F_0 = 5$ eV, $F_2 = 6$ eV) evidences that copper and oxygen Dzyaloshinsky vectors

can be of comparable magnitude.

D. Dzyaloshinsky-Moriya coupling in La_2CuO_4

The DM coupling and magnetic anisotropy in La_2CuO_4 and related compounds has attracted considerable attention in 90-ths (see, e.g., Refs.7,8,9), and is still debated in the literature.[11,12] In the low-temperature tetragonal (LTT) and orthorhombic (LTO) phases of La_2CuO_4, the oxygen octahedra surrounding each copper ion rotate by a small tilting angle ($\delta_{LTT} \approx 3^0, \delta_{LTO} \approx 5^0$) relative to their location in the high-temperature tetragonal phase. The structural distortion allows for the appearance of the antisymmetric Dzyaloshinsky-Moriya interaction. In terms of our choice for structural parameters to describe the Cu_1-O-Cu_2 bond we have for LTT phase: $\theta = \pi; \delta_1 = \delta_2 = \frac{\pi}{2} \pm \delta_{LTT}$ for bonds oriented perpendicular to the tilting plane, and $\theta = \pm(\pi - 2\delta_{LTT}); \delta_1 = \delta_2 = \frac{\pi}{2}$ for bonds oriented parallel to the tilting plane. It means that all the local Dzyaloshinsky vectors turn into zero for the former bonds, and turn out to be perpendicular to the tilting plane for the latter bonds. For LTO phase:$\theta = \pm(\pi - \sqrt{2}\delta_{LTO}); \delta_1 = \delta_2 = \frac{\pi}{2} \pm \delta_{LTO}$. In such a case the largest ($\propto \delta_{LTO}$) component of the local Dzyaloshinsky vectors (z-component in our notation) turn out to be oriented perpendicular to the Cu_1-O-Cu_2 bond plane. Other two components of the local Dzyaloshinsky vectors are fairly small: that of perpendicular to CuO_2 plane (y-component in our notation) is of the order of δ^2_{LTO}, while that of oriented along Cu_1-Cu_2 bond axis (x-components in our notation) is of the order of δ^3_{LTO}.

IV. DM COUPLED CU_1-O-CU_2 BOND IN EXTERNAL FIELDS

A. Uniform external magnetic field

Application of an uniform external magnetic field $\mathbf{h}_S$ will produce a staggered spin polarization in the antiferromagnetically coupled Cu_1-Cu_2 pair

$$\langle \mathbf{V}_{12} \rangle = \mathbf{L} = -\frac{1}{J^2_{12}}[\sum_i \mathbf{D}^{(i)}_{12} \times \mathbf{h}^S] = \overleftrightarrow{\chi}^{VS} \mathbf{h}^S \qquad (25)$$

with antisymmetric VS-susceptibility tensor: $\chi^{VS}_{\alpha\beta} = -\chi^{VS}_{\beta\alpha}$. One sees that the sense of a staggered spin polarization, or antiferromagnetic vector, depends on that of Dzyaloshinsky vector.[26] The VS coupling results in many interesting effects for the DM systems, in particular, the "field-induced gap" phenomena in 1D s=1/2 antiferromagnetic Heisenberg system with alternating DM coupling.[6] Approximately, the phenomenon is described by a so called *staggered* s=1/2 antiferromagnetic Heisenberg model with the Hamiltonian

$$\hat{H} = J\sum_i (\hat{\mathbf{s}}_i \cdot \hat{\mathbf{s}}_{i+1}) - h_u \hat{s}_{iz} - (-1)^i h_s \hat{s}_{ix}\,, \qquad (26)$$

which includes the effective uniform field h_u and the induced staggered field $h_s \propto h_u$ perpendicular both to the applied uniform magnetic field and Dzyaloshinsky vector.

B. Staggered external field

Application of a staggered field $\mathbf{h}^V$ for an antiferromagnetically coupled Cu_1-Cu_2 pair will produce a local spin polarization both on copper and oxygen sites

$$\langle \mathbf{S}_i \rangle = \frac{1}{J^2_{12}}[\mathbf{D}^{(i)}_{12} \times \mathbf{h}^V] = \overleftrightarrow{\chi}^{SV}(i)\mathbf{h}^V, \qquad (27)$$

which can be detected by different site-sensitive methods including neutron diffraction and, mainly, by nuclear magnetic resonance. It should be noted that SV-susceptibility tensor is the antisymmetric one: $\chi^{SV}_{\alpha\beta} = -\chi^{SV}_{\beta\alpha}$. Strictly speaking, both formulas (25),(27) work well only in a paramagnetic regime and for relatively weak external fields.

Above we addressed a single Cu_1-O-Cu_2 bond, where, despite a site location, the direction and magnitude of Dzyaloshinsky vector depends strongly on the bond strength and geometry. It is clear that a site rather than a bond location of DM vectors would result in a revisit of conventional symmetry considerations and of magnetic structure in weak ferro- and antiferromagnets. Interestingly that the expression (27) predicts the effects of a constructive or destructive (frustration) interference of copper spin polarizations in 1D, 2D, and 3D lattices depending on the relative sign of Dzyaloshinsky vectors and staggered fields for nearest neighbours. It should be noted that with the destructive interference the local copper spin polarization may turn into zero and DM coupling will manifest itself only through the oxygen spin polarization. Another interesting manifestation of oxygen Dzyaloshinsky-Moriya antisymmetric exchange coupling concerns the edge-shared CuO_2 chains (see Fig.2), ubiquitous in many cuprates, where we deal with an exact compensation of copper contributions to Dzyaloshinsky vectors and the possibility to observe the effects of uncompensated though oppositely directed local oxygen contributions. Applying the staggered field along chain direction (O_x) we arrive in accordance with Exp.(27) at a *weakly* antiferromagnetic O_y ordering of oxygen spin polarizations which magnitude is expected to be strongly enhanced due to usually small magnitudes of 90^o symmetric superexchange. It should be emphasized that the summary Dzyaloshinsky vector turns into zero hence in terms of a conventional approach to DM theory we miss the anomalous oxygen spin polarization effect. In this connection it is worth noting the neutron diffraction data

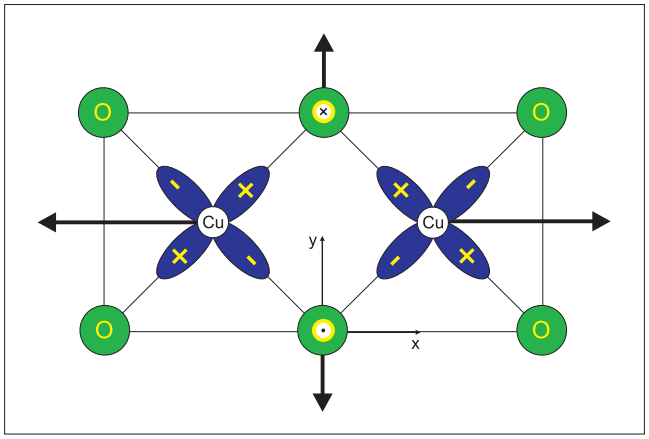

FIG. 2: The fragment of a typical edge-shared CuO_2 chain with copper and oxygen spin orientation under staggered field applied along x-direction. Note the antiparallel orientation of oxygen Dzyaloshinsky vectors.

by Chung *et al.*[27] which unambiguously evidence the oxygen momentum formation and canting in edge shared CuO_2 chain cuprate Li_2CuO_2.

C. Intermediate oxygen ^{17}O Knight shift as an effective tool to inspect DM coupling for Cu-O-Cu bonds

As an important by-product of the cuprate activity we arrived at a significant progress in different experimental methods and new opportunities to elucidate subtle details of electron and spin structure. In particular, it concerns the oxygen ^{17}O NMR-NQR as an unique local probe to study the charge and spin densities on oxygen sites.[13] In this connection we point to papers by R. Walstedt *et al.*[13] as a first direct observation of anomalous oxygen hyperfine interactions in generic cuprate La_2CuO_4. With the approaching transition to the ordered magnetic phase, the authors observed anomalously large negative ^{17}O Knight shift for planar oxygens which anisotropy resembled that of weak ferromagnetism in this cuprate. The giant shift was observed only when external field was parallel to the local Cu-O-Cu bond axis (PL1 lines) or perpendicular to CuO_2 plane. The effect was not observed for PL2 lines which correspond to oxygens in the local Cu-O-Cu bonds which axis is perpendicular to in-plane external field. The data were interpreted as an indication of oxygen spin polarization due to a local Dzyaloshinsky-Moriya antisymmetric exchange coupling. However, either interpretation of NMR-NQR data in such low-symmetry systems as La_2CuO_4 needs in a thorough analysis of transferred hyperfine interactions and a revisit of some textbook results being typical for the model high-symmetry systems. First we draw attention to spin-dipole hyperfine interactions for O 2p-holes which are main participants of Cu_1-O-Cu_2 bonding. Starting from a conventional formula for a spin-dipole contribution to local field

$$\mathcal{H}_n = -g_s\mu_B \sum_i \frac{3(\mathbf{r}_i\cdot\mathbf{s}_i)\mathbf{r}_i - r_i^2\mathbf{s}_i}{r_i^5}$$

and making use of an expression for appropriate matrix element

$$\langle p_i|\frac{3x_\alpha x_\beta - r^2\delta_{\alpha\beta}}{r^5}|p_j\rangle = -\frac{2}{5}\left\langle\frac{1}{r^3}\right\rangle_{2p}\langle p_i|3\widetilde{l_\alpha l_\beta}-2\delta_{\alpha\beta}|p_j\rangle =$$

$$\frac{2}{5}\left\langle\frac{1}{r^3}\right\rangle_{2p}(\frac{3}{2}\delta_{\alpha i}\delta_{\beta j}+\frac{3}{2}\delta_{\alpha j}\delta_{\beta i}-\delta_{\alpha\beta}\delta_{ij}) \qquad (28)$$

we present a local field on the ^{17}O nucleus in Cu_1-O-Cu_2 system as a sum of ferro- and antiferromagnetic contributions as follows[26]

$$\mathcal{H}_n = \overleftrightarrow{\mathbf{A}}^S\cdot\langle\hat{\mathbf{S}}\rangle + \overleftrightarrow{\mathbf{A}}^V\cdot\langle\hat{\mathbf{V}}\rangle \qquad (29)$$

where

$$\overleftrightarrow{\mathbf{A}}^S = \overleftrightarrow{\mathbf{A}}^S(dp)+\overleftrightarrow{\mathbf{A}}^S(pd);\ \overleftrightarrow{\mathbf{A}}^V = \overleftrightarrow{\mathbf{A}}^V(pd)-\overleftrightarrow{\mathbf{A}}^V(dp),$$

$$A^S_{ij}(dp) = A_p^{(0)}[3c_t(dp_i)c_t(dp_j)-|\mathbf{c}_t(dp)|^2\delta_{ij}],$$

$$A^S_{ij}(pd) = A_p^{(0)}[3c_t(p_id)c_t(p_jd)-|\mathbf{c}_t(pd)|^2\delta_{ij}],$$

$$A^V_{ij}(dp) = A_p^{(0)}[3c_s(dp_i)\widetilde{c_t}(dp_j)-(\mathbf{c}_s(dp)\cdot\mathbf{c}_t(dp))\delta_{ij}],$$

$$A^V_{ij}(pd) = A_p^{(0)}[3c_s(p_i\widetilde{d})c_t(p_jd)-(\mathbf{c}_s(pd)\cdot\mathbf{c}_t(pd))\delta_{ij}],$$

where $A_p^{(0)} = \frac{2}{5}g_s\mu_B\left\langle\frac{1}{r^3}\right\rangle_{2p}$, the tilde points to a symmetrization. Thus, along with a conventional textbook ferromagnetic ($\propto\langle\hat{\mathbf{S}}\rangle$) transferred hyperfine contribution to local field which simply mirrors a sum total of two Cu-O bonds, we arrive at an additional unconventional antiferromagnetic difference ($\propto\langle\hat{\mathbf{V}}\rangle$) contribution which symmetry and magnitude strongly depend on the orientation of the oxygen crystal field axes and Cu_1-O-Cu_2 bonding angle. With the Cu_1-O-Cu_2 geometry shown in Fig.1 we arrive at a diagonal $\overleftrightarrow{\mathbf{A}}^S$ tensor:

$$A^S_{xx} = 2A_p(3\sin^2\frac{\theta}{2}-1);\ A^S_{yy} = 2A_p(3\cos^2\frac{\theta}{2}-1);\ A^S_{zz} = -2A_p,$$

and the only nonzero components of $\overleftrightarrow{\mathbf{A}}^V$ tensor:

$$A^V_{xy} = A^V_{yx} = 3A_p\sin\theta$$

with

$$A_p = \frac{3}{4}\left(\frac{t_{dp\sigma}}{\epsilon_p}\right)^2 A_p^0 = f_\sigma A_p^0,$$

where f_σ is the parameter of a transferred spin density and we made use of a simple approximation $E_{s,t}(dp_{x,y}) \approx \epsilon_p$. Generally speaking, we should take into account an additional contribution of magneto-dipole hyperfine interactions.

The two-term structure of oxygen local field implies a two-term S-V structure of the ^{17}O Knight shift

$$^{17}K = \overleftrightarrow{\mathbf{A}}^{S} \overleftrightarrow{\chi}^{SS} + \overleftrightarrow{\mathbf{A}}^{V} \overleftrightarrow{\chi}^{VS}$$

that points to Knight shift as an effective tool to inspect both uniform and staggered spin polarization. The existence of antiferromagnetic term in oxygen hyperfine interactions yields a rather simple explanation of the ^{17}O Knight shift anomalies in La_2CuO_4[13] as a result of the external field induced staggered spin polarization $\langle \hat{\mathbf{V}} \rangle = \mathbf{L} = \overleftrightarrow{\chi}^{\mathbf{VS}} \mathcal{H}_{\mathbf{ext}}$. Indeed, "our" local y axis for Cu_1-O-Cu_2 bond corresponds to the crystal tetragonal c-axis oriented perpendicular to CuO_2 planes both in LTO and LTT phases of La_2CuO_4 while x-axis does to local Cu-O-Cu bond axis. It means that for the geometry of the experiment by Walstedt *et al.*[13] (the crystal is oriented so that the external uniform field is either $\parallel$ or $\perp$ to the local Cu-O-Cu bond axis) the antiferromagnetic contribution to ^{17}O Knight shift will be observed only a) for oxygens in Cu_1-O-Cu_2 bonds oriented along external field or b) for external field along tetragonal c-axis. Experimental data[13] agree with staggered magnetization along the tetragonal c-axis in the former and along the rhombic c-axis (tetragonal ab-axis) in the latter. Interestingly, the sizeable effect has been observed in La_2CuO_4 for temperatures $T \sim 500$ K that is essentially higher than $T_N \approx 300$ K. Given $L = 1$, $A_p^{(0)} \approx 100$ kG/spin,[13] $|\sin\theta| \approx 0.1$, and $f_\sigma \approx 20\%$ we obtain ≈ 6 kG as a maximal value of a low-temperature antiferromagnetic contribution to hyperfine field which is parallel to external magnetic field. This value agrees with a low-temperature extrapolation of high-temperature experimental data by Walstedt *et al.*[13] Similar effect of anomalous ^{13}C Knight shift has recently been observed in copper pyrimidine dinitrate $[CuPM(NO_3)_2(H_2O)_2]_n$, a one-dimensional S=1/2 antiferromagnet with alternating local symmetry.[32] However, the authors did take into account only the inter-site magneto-dipole contribution to $\overleftrightarrow{\mathbf{A}}^{V}$ tensor that questions their quantitative conclusions regarding the "giant" spin canting.

The ferro-antiferromagnetic S-V structure of local field on the nucleus of an intermediate oxygen ion in a Cu_1-O-Cu_2 triad points to ^{17}O NMR as, probably, the only experimental technique to measure both the value, direction, and the sense of Dzyaloshinsky vector. The latter possibility was realized earlier with ^{19}F NMR for weak ferromagnet FeF_3.[26] The experimental observation of antiferromagnetic contribution to the Knight shift provides probably the sole way to find out the problem of the sense of Dzyaloshinsky vector in cuprates. For instance, the negative sign of ^{17}O Knight shift in La_2CuO_4[13] points to a negative sign of $\overleftrightarrow{\chi}^{VS}$ for Cu_1-O-Cu_2 triad with $A^V_{xy} > 0$, hence to a positive sense of z-component of the summary Dzyaloshinsky vector in Cu_1-O-Cu_2 triad with geometry shown in Fig.1 given $\theta \leq \pi$, $\delta_1 = \delta_2 \approx \pi/2$. This agrees with theoretical predictions both for copper and oxygen contributions based on Exps.(17) and (21). It should be emphasized that the above effect is determined by the summary Dzyaloshinsky vector in Cu_1-O-Cu_2 triad rather than by a local oxygen "weak-ferromagnetic" polarization as it was proposed by Walstedt *et.al.*[13]

V. SYMMETRIC SPIN ANISOTROPY

Symmetric spin anisotropy for a Cu_1-Cu_2 pair is described by an effective Hamiltonian

$$\hat{H}_{an} = \frac{1}{4}\hat{\mathbf{S}}\overleftrightarrow{\mathbf{K}}^{S}\hat{\mathbf{S}} - \frac{1}{4}\hat{\mathbf{V}}\overleftrightarrow{\mathbf{K}}^{V}\hat{\mathbf{V}} \tag{30}$$

with kinematic relations (7).

Depending on the sign of the anisotropy constants we arrive at two types of spin configurations minimizing the energy of spin anisotropy: the conventional twofold degenerated ferromagnetic state or unconventional multiple degenerated antiferromagnetic state. As a relevant illustrative example one might refer to the axial anisotropy: $\hat{H}_{an} = K\hat{S}_z^2$ which stabilizes the $|1 \pm 1\rangle$ doublet given $K < 0$ or a set of superposition states

$$\Psi_{\alpha,\phi} = \cos\alpha|00\rangle + e^{i\phi}\sin\alpha|10\rangle \tag{31}$$

given $K > 0$. The latter incorporates the limiting configurations $|00\rangle$ and $|10\rangle$, the Néel ($\frac{1}{\sqrt{2}}(|00\rangle \pm |10\rangle)$) and DM doublets ($\frac{1}{\sqrt{2}}(|00\rangle \pm i|10\rangle)$), and any other their superpositions.

As usual, the term is processed in frames of a number of simple model approximations. First, instead of the generalized form (30) one addresses a pseudodipole anisotropy

$$\hat{H}_{an} = \hat{\mathbf{s}}_1\overleftrightarrow{\mathbf{K}}_{12}\hat{\mathbf{s}}_2\,. \tag{32}$$

Second, one makes use of a trivial local MFA approach which applicability for s=1/2 spin systems is questionable. Indeed, calculating the classical energy of the pseudodipole two-ion anisotropy $K\langle\hat{s}_{1z}\rangle\langle\hat{s}_{2z}\rangle = \frac{1}{4}K(\langle\hat{S}_z\rangle^2 - \langle\hat{V}_z\rangle^2)$ and respective quantum energy $K\langle\hat{s}_{1z}\hat{s}_{2z}\rangle = \frac{1}{4}K(\langle\hat{S}_z^2\rangle - \langle\hat{V}_z^2\rangle)$ for a two-ion state $\cos\alpha|00\rangle + \sin\alpha|1n\rangle$ induced by a Néel-like staggered field $\mathbf{h}^V \parallel \mathbf{n}$ we arrive at $E_{class} = -\frac{1}{4}K\sin 2\alpha \cdot n_z^2$ and $E_{quant} = \frac{1}{4}K(1 - 2\sin^2\alpha \cdot n_z^2)$, respectively, that evidences the crucial importance of quantum effects when addressing the numerical aspect of spin anisotropy. Note that the mean value $\langle\hat{V}_z^2\rangle$ reaches the maximum (=1) on a set of superposition states (31), while $\langle\hat{V}_z\rangle^2$ does on a single Néel state $\Psi_{\alpha=\pi/4,\phi=0}$.

A. Effective symmetric spin anisotropy due to DM interaction

When one says about an effective spin anisotropy due to DM interaction one usually addresses a simple classical two-sublattice weak ferromagnet where the free energy has a minimum when both ferro- ($\propto \langle\hat{\mathbf{S}}\rangle$) and antiferromagnetic ($\propto \langle\hat{\mathbf{V}}\rangle$) vectors, being perpendicular to each other, lie in the plane perpendicular to Dzyaloshinsky vector $\mathbf{D}$. However, the issue is rather involved and appeared for a long time to be hotly debated.[9,10,29,30] In our opinion, first of all we should define what spin anisotropy is. Indeed, the description of any spin system implies the free energy Φ depends on a set of vectorial order parameters (e.g.,$\langle\hat{\mathbf{S}}\rangle, \propto \langle\hat{\mathbf{V}}\rangle, \propto \langle\hat{\mathbf{T}}\rangle$) under kinematic constraint, rather than a single magnetic moment as in a simple ferromagnet, that can make the orientational dependence of Φ extremely involved. Such a situation needs in a careful analysis of respective spin Hamiltonian with a choice of proper approximations.

Effective symmetric spin anisotropy due to DM interaction can be easily derived as a second order perturbation correction due to DM coupling as follows:

$$\hat{H}_{an}^{DM} = \hat{P}\hat{H}_{DM}\hat{R}\hat{H}_{DM}\hat{P}\,,$$

where $\hat{P}$ is the projection operator projecting on the ground manifold and $\hat{R} = (1-\hat{P})/(E_0 - \hat{H}_0)$. For antiferromagnetically coupled spin 1/2 pair $\hat{H}_{an}^{DM}$ may be written as follows:

$$\hat{H}_{an}^{DM} = \sum_{ij} \Delta K_{ij}^{V} \hat{V}_i \hat{V}_j$$

with $\Delta K_{ij}^{V} = \frac{1}{8J} D_i D_j$ provided $|\mathbf{D}| \ll J$. We see that in frames of a simple MFA approach this anisotropy stabilizes a Néel state with $\langle\hat{\mathbf{V}}\rangle \perp \mathbf{D}$. However, in fact we deal with an MFA artefact. Indeed, let examine the second order perturbation correction to the ground state energy of an antiferromagnetically coupled spin 1/2 pair in a Néel-like staggered field $\mathbf{h}^V \parallel \mathbf{n}$:

$$E_{an}^{DM} = -\frac{|\mathbf{D}\cdot\mathbf{n}|^2}{4(E_\parallel - E_g)} - \frac{|\mathbf{D}\times\mathbf{n}|^2}{4(E_\perp - E_g)}\cos^2\alpha\,, \qquad (33)$$

where $E_\perp = J; E_\parallel = J\cos^2\alpha + h^V \sin 2\alpha; E_g = J\sin^2\alpha - h^V \sin 2\alpha$. First term in (33) stabilizes $\mathbf{n} \parallel \mathbf{D}$ configuration while the second one does the $\mathbf{n} \perp \mathbf{D}$ configuration. Interestingly that $(E_\parallel - E_g)\cos^2\alpha = (E_\perp - E_g)$, that is for any staggered field E_{an}^{DM} does not depend on its orientation. In other words, at variance with a simple MFA approach, the DM contribution to the energy of anisotropy for an exchange coupled spin 1/2 pair in a staggered field turns into zero. The conclusion proves to be correct in the limit of a zero field as well.

B. Microscopics of symmetric spin anisotropy

Anyway, the $\hat{H}_{an}^{DM}$ term has not to be included into an effective spin anisotropy Hamiltonian (6). As concerns the true symmetric two-ion spin anisotropy (pseudodipole, or exchange anisotropy), its magnitude can be obtained if we take into account all other effects quadratic in spin-orbital coupling.

At variance with the effective DM spin-Hamiltonian the symmetric spin anisotropy evolves from the higher-order perturbation effects that makes its analysis even more involved and leads to many misleading estimations. Similarly to DM interaction we deal with two competing contributions. The first is derived as a lowest order contribution which does not take account of orbital fluctuations for $Cu_{1,2}$ 3d states. To this end we take into account the effects of spin-orbital mixing for ground state singlet and triplet 101 configurations perturbed by covalent effects. Assuming the validity of conventional perturbation series we arrive at a modified expression for respective functions as follows

$$\Psi_{101;SM} = \Phi_{101;SM} + \sum_{\{n\}\Gamma} c_{\{n\}}({}^{2S+1}\Gamma)\left[\Phi_{\{n\};\Gamma SM} - \sum_{S'M'\Gamma'} \frac{\langle\{n\};\Gamma' S' M'|V_{so}|\{n\};\Gamma SM\rangle}{E_{2S'+1\Gamma'}(\{n\}) - E_{2S+1\Gamma_0}(101)}\Phi_{\{n\};\Gamma' S' M'}\right] \qquad (34)$$

and arrive at the expressions for the tensorial anisotropy parameters as follows:

$$K_{ij}^{S} = \sum_{\{n\}\Gamma_1,\Gamma_2,\Gamma'} c_{\{n\}}^{*}({}^3\Gamma_1) c_{\{n\}}({}^3\Gamma_2) \frac{\langle\{n\};{}^3\Gamma_1|\Lambda_i^S|\{n\};{}^3\Gamma'\rangle\langle\{n\};{}^3\Gamma'|\Lambda_j^S|\{n\};{}^3\Gamma_2\rangle}{E_{^3\Gamma'}(\{n\}) - E_{^3\Gamma_0}(101)}, \qquad (35)$$

$$K_{ij}^{V}=\sum_{\{n\}\Gamma_1,\Gamma_2,\Gamma'} c^{*}_{\{n\}}({}^3\Gamma_1)c_{\{n\}}({}^3\Gamma_2)\frac{\langle\{n\};{}^3\Gamma_1|\Lambda_i^V|\{n\};{}^1\Gamma'\rangle\langle\{n\};{}^1\Gamma'|\Lambda_j^V|\{n\};{}^3\Gamma_2\rangle}{E_{{}^1\Gamma'}(\{n\})-E_{{}^3\Gamma_0}(101)}. \quad (36)$$

We see that K_{ij}^S and K_{ij}^V are determined by the triplet-triplet and singlet-triplet mixing, respectively. Interestingly that for nonzero orbital matrix elements in (35) and (36) we find

$$\langle\{n\};{}^3\Gamma_1|\Lambda_i^S|\{n\};{}^3\Gamma'\rangle=\langle\{n\};{}^3\Gamma_1|\Lambda_i^V|\{n\};{}^1\Gamma'\rangle$$

hence $K_{ij}^S=K_{ij}^V$, if we will suppose that $E_{{}^1\Gamma'}(\{n\})=E_{{}^3\Gamma'}(\{n\})$, that is neglect the singlet-triplet splitting for Γ' terms, or respective exchange effects. It should be noted that the contribution of two-hole on-site 200, 002, and 020 configurations in (35) and (36) is actually related to an on-site, or single ion spin anisotropy. Thus we conclude that, strictly speaking, a simple two-site pseudodipole form of symmetric anisotropy (1) fails to capture correctly all the features of spin anisotropy in our three-center two-hole system. Firstly it concerns the quantitative predictions and estimations. The contribution of two-hole two-site 110 and 011 configurations to spin anisotropy turns out to be nonzero, only if pd-exchange is taken into account.

The second contribution is associated with orbital fluctuations for $Cu_{1,2}$ 3d states within a ground state 101 configuration, and evolves from a third order combined effect of $Cu_{1,2}$ spin-orbital $V_{so}(Cu_{1,2})$ and effective Cu_1-Cu_2 exchange coupling (see, e.g., a detailed analysis in Ref.28). Thus, we see that any decisive conclusions regarding the quantitative estimations of symmetric spin anisotropy imply a thorough analysis of numerous competing contributions.

VI. CONCLUSIONS

In conclusion, we have revisited a problem of Dzyaloshinsky-Moriya antisymmetric exchange coupling in cuprates specifying the local spin-orbital contributions to Dzyaloshinsky vector focusing on the oxygen term. We have applied a scheme that provides an optimal way to account for intra-atomic electron correlations and separate the local contributions to Dzyaloshinsky vector. The Dzyaloshinsky vector and respective weak ferromagnetic momentum is shown to be a superposition of comparable and, sometimes, competing local Cu and O contributions. The intermediate oxygen ^{17}O Knight shift is shown to be an effective tool to inspect the effects of Dzyaloshinsky-Moriya coupling in an external magnetic field. Anisotropic antiferromagnetic contribution to ^{17}K explains the anomalies observed in La_2CuO_4.[13] We predict the effect of *strong* oxygen weak antiferromagnetism in edge-shared CuO_2 chains due to uncompensated oxygen Dzyaloshinsky vectors. Its experimental observation could provide a direct evidence of the oxygen DM coupling. We revisit the effects of symmetric spin anisotropy, in particular, those directly induced by Dzyaloshinsky-Moriya coupling.

Finally it should be noted that the anionic contribution to Dzyaloshinsky vector is crucial for the very existence of the DM coupling in the pair of rare-earth ions (see, e.g., Yb^{3+}-As^{4-}-Yb^{3+} triads in Yb_4As_3[31]) because very strong spin-orbital coupling for rare-earth ions is diagonalized within a ground state multiplet.

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