Dzyaloshinskii-Moriya interaction in the cuprates

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The Dzyaloshinskii-Moriya interaction, which arises from a mixture of superexchange and spin-orbit coupling NN Cu^{2+} spin with a term of the $\mathbf{D}_{ij}\cdot(\mathbf{S}_i\times\mathbf{S}_j)$. The coupling constants $\mathbf{D}_{ij}$ are estimated for several cuprate crystal structures. The pattern of the $\mathbf{D}_{ij}$ varies considerably between these structures and only in some cases causes a weak ferromagnetic component in an ordered antiferromagnetic of the Cu spins. In no case, however, does this interaction stabilize a flux phase.

I. INTRODUCTION

The combination of low symmetry and spin-orbit coupling was shown by Dzyaloshinskii[1] and Moriya[2] some 30 years ago to give rise to an anisotropic exchange interaction. In the case of the cuprates this Dzyaloshinskii-Moriya (DM) interaction is the leading source of anisotropy, since single-site anisotropy does not occur due to the $S=\frac{1}{2}$ nature of the spins on the Cu^{2+} sites. Thio *et al.*[3] invoked this interaction to explain the small net ferromagnetic component to the ordered moments in the orthorhombic phase of La_2CuO_4.[4] More recently Thio *et al.*[5] pointed out that, because of the extreme sensitivity of the pattern of the DM interactions to the crystal structure, it would be one of the few interactions that differ in the closely related orthorhombic and low-temperature tetragonal structures found in the compounds $La_{2-x}Ba_xCuO_4$. Since the transition between these two crystal structures was shown by Axe *et al.*[6] and by Maeno *et al.*[7] to cause a dramatic suppression of the transition for superconductivity, it is of some interest to look into this question further.

Recently Coffey, Bedell, and Trugman[8] made a complete examination of the pattern of DM coupling constants in the orthorhombic phase based on a symmetry analysis. The microscopic basis for the DM interaction has been known since the work of Moriya,[2] and in this paper we apply Moriya's method to the case of a Cu^{2+}—O—Cu^{2+} bond in which the Cu ions are surrounded by tilted O octahedra. The result is a small DM interaction, which depends linearly on the tilt of the O octahedra and on the spin orbit of the Cu^{2+} ions. The form agrees with the previous analysis, and the details of the microscopic calculation for the orthorhombic La_2CuO_4 structure are given in Sec. II.

The pattern of the DM interaction vectors, $\mathbf{D}_{ij}$, is sensitive to the deviations from the ideal tetragonal La_2CuO_4 structure. Thus the two cases of orthorhombic La_2CuO_4 with alternating tilted O octrohedra in $\langle 110\rangle$ directions and low-temperature tetragonal $La_{2-x}Ba_xCuO_4$ with tilted O octahedra in $\langle 110\rangle$ directions have quite different patterns, as pointed out by Thio *et al.*[8] In Sec. III we discuss the patterns for these two cases in detail and also for the case of $YB_2Cu_3O_6$. To illustrate the physical consequences of these different patterns we examine their effect on an antiferromagnetically ordered state and show that only in the first case of the orthorhombic structure does the DM interaction induce a small ferromagnetic moment.

Our conclusions are presented in Sec. IV, where also discuss the relationship between the flux phases and a DM interaction.

II. MICROSCOPIC ORIGIN OF THE DZYALOSHINSKII-MORIYA INTERACTION IN ORTHORHOMBIC La_2CuO_4

The standard theory of superexchange, due to Anderson,[9] must be modified in the presence of spin-orbit coupling. Moriya[2] has shown how the processes involving an additional virtual transition due to the spin-orbit interaction can cause an anisotropic exchange interaction as a correction to the isotropic Anderson superexchange term. To illustrate this process for the cuprates, we consider the case of orthorhombic La_2CuO_4. In Fig. 1 we illustrate a CuO_2 plane in this structure.[4] The O octahedra are tilted alternately along [110] and [1$\bar{1}$0] directions so that lines of O ions ||[110] are alternately slightly raised or depressed relative to the (001) plane defined by the Cu ions. The crystal-field states of the Cu^{2+} ions are rotated and defined by the local O octahedra.

We consider an individual Cu—O—Cu bond and the relevant Hamiltonian consists of the crystal-field levels of the 3d hole that forms the Cu^{2+} ions and the antibonding

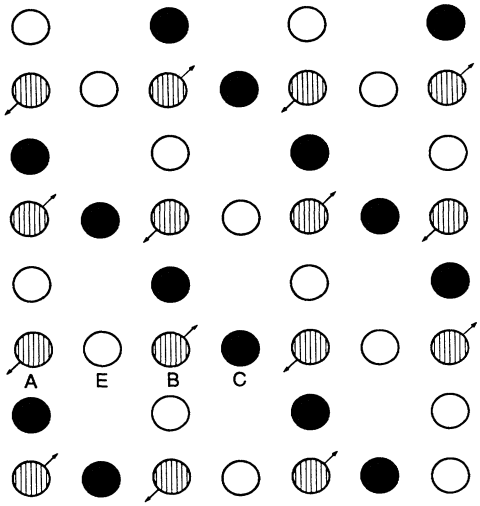

FIG. 1. Here only the oxygen sites are shown. The open circles are oxygen atoms which are tilted up out of the Cu plane, the solid circles are oxygen atoms tilted down out the Cu plane, and the hatched circles are oxygen sites in the Cu plane. The Cu sites are underneath the circles with the arrows, which are the positions of the apical oxygens. The arrows indicate the direction in which these oxygen atoms move.

$2p_\sigma$ level of the O,[10] and in addition the spin-orbit coupling on the Cu atoms:

$$H = H_0 + H_t + H_{LS} \tag{1}$$

with single-site terms

$$H_0 = \sum_{j\sigma} \sum_{\alpha=0,m} \varepsilon_{j\alpha} d^\dagger_{j\alpha\sigma} d_{j\alpha\sigma} + \sum_{k\sigma} \varepsilon_p p^\dagger_{k\sigma} p_{k\sigma} + U \sum_{j\alpha\alpha'} d^\dagger_{j\alpha\uparrow} d^\dagger_{j\alpha'\downarrow} d_{j\alpha'\downarrow} d_{j\alpha\uparrow} , \tag{2}$$

nearest-neighbor hybridization terms

$$H_t = \sum_{j,\alpha,\sigma} \sum_{k\in\{j\}} (t_\alpha d^\dagger_{j\alpha\sigma} p_{k\sigma} + \text{H.c.}) , \tag{3}$$

and spin-orbit terms

$$H_{LS} = \lambda \sum_j \mathbf{L}_j \cdot \mathbf{S}_j = \frac{\lambda}{2} \sum_j (L_j^+ S_j^- + L_j^- S_j^+ + 2L_j^z S_j^z) . \tag{4}$$

The notation is standard and the only new terms involve the crystal fields of the 3d hole denoted by $\alpha=0$ (ground-state energy $\varepsilon_0=0$) and $\alpha=m$ (excited-state energy $\varepsilon_m > 0$). The standard Anderson superexchange is obtained in perturbation theory by eliminating the hybridization term to obtain an effective Heisenberg interaction between the Cu^{2+} spins, which is $O(t^4)$.[10] Moriya[2] considered the lowest-order correction to this process, which involves a single power of the spin-orbit coupling. If we use second-order perturbation theory to eliminate the excited crystal-field levels, we get an additional vector hybridization term

$$H_v = \sum_k \sum_{j\in\{k\}} \mathbf{C}_{kj} \cdot \mathbf{S}_{kj} + \text{H.c.} , \tag{5}$$

where

$$\mathbf{C}_{kj} = -\frac{\lambda}{2} \sum_m \frac{\mathbf{L}_{mo}(j)}{\varepsilon_m} t_m \tag{6}$$

and

$$S^+_{kj} = p^\dagger_{k\uparrow} d_{j0\downarrow}, \quad S^-_{kj} = p^\dagger_{k\downarrow} d_{j0\uparrow}, \quad S^z_{kj} = p^\dagger_{k\uparrow} d_{j0\downarrow} - p^\dagger_{k\downarrow} d_{j0\uparrow} . \tag{7}$$

At this stage we have an effective Hamiltonian, which involves only the ground-state crystal-field levels in H_0 and $H_t + H_v$ as hybridization terms. The vector coupling constants $\mathbf{C}_{kj}$ are obtained by examining the matrix elements of the $\mathbf{L}$ vector involving the ground-state crystal-field level. Consider the combination in Fig. 1. $k=E$, $j=A$. The tilting of the O octahedra causes a small admixture d_{xz} and d_{yx} orbitals to the $d_{x^2-y^2}$ orbital, so we obtain

$$|O_A\rangle = |d_{x^2-y^2}\rangle + \alpha\theta(|d_{xz}\rangle - |d_{yz}\rangle) , \tag{8}$$

where θ is the angle between the vector AE and the (001) plane. Because of the tilt, there is a small overlap of the d_{xz} orbital and p_σ orbital at E, and this determines the size of the admixing $\alpha\theta = t_{xz}/t_0$. The nonzero matrix elements of $\mathbf{L}$ are

$$\langle d_{xz}|\mathbf{L}|O_A\rangle = -i\hat{\mathbf{y}}, \quad \langle d_{yz}|\mathbf{L}|O_A\rangle = i\hat{\mathbf{x}} , \quad \langle d_{r^2-3z^2}|\mathbf{L}|O_A\rangle = \alpha\theta\sqrt{3}i(\hat{\mathbf{x}}+\hat{\mathbf{y}}) . \tag{9}$$

Putting these terms together, we arrive at the result

$$\mathbf{C}_{EA} = \frac{i\lambda}{2} \left[\frac{\sqrt{3}\alpha\theta}{\varepsilon_{r^2-3z^2}} t_{r^2-3z^2}(\hat{\mathbf{x}}+\hat{\mathbf{y}}) - \frac{t_{xz}}{\varepsilon_{xz}} \hat{\mathbf{y}} \right] , \tag{10}$$

where $t_{r^2-3z^2}$, t_{zx} are real. The two terms parallel to $\mathbf{y}$ have the same order of magnitude, since t_{xz} is proportional to θ, but they have opposite signs. By symmetry $\mathbf{C}_{EB} = -\mathbf{C}_{EA}$.

Lastly we eliminate the p_σ orbitals from Eqs. (2)–(5) and obtain an expression in perturbation theory for the DM coupling

$$H_{D-M} = \sum_{\langle ij \rangle} \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j) \tag{11}$$

with the vector coupling constant

$$\mathbf{D}_{ij} = -\frac{8t_0^3}{\varepsilon_p^2} \left[\frac{1}{\varepsilon_p} + \frac{1}{U} \right] (\mathbf{C}_{ik} - \mathbf{C}_{ki} + \mathbf{C}_{kj} - \mathbf{C}_{jk}) , \tag{12}$$

where k is the O site between i and j. Note $\mathbf{C}_{jk} = \mathbf{C}^*_{kj}$ so that the DM coupling constant is real.

For the specific case of $\mathbf{D}_{AB}$ we arrive at the result

$$\mathbf{D}_{AB} = -\frac{8\lambda t_0^3}{\varepsilon_p^2} \left[\frac{1}{\varepsilon_p} + \frac{1}{U} \right] \left[\frac{\sqrt{3}\alpha\theta}{\varepsilon_{r^2-3z^2}} t_{r^2-3z^2}(\hat{\mathbf{x}}+\hat{\mathbf{y}}) - \frac{t_{xz}}{\varepsilon_{xz}} \hat{\mathbf{y}} \right] . \tag{13}$$

The coupling constant for the nearest Cu—O bonds are reversed, i.e., $\mathbf{D}_{BC}=-\mathbf{D}_{AB}$ leading to the alternating pattern of coupling vectors found on general symmetry grounds by Coffey, Bedell, and Trugman.[8]

The angle the spins make with the Cu plane is given by[11]

$$\phi=\frac{1}{2}\tan^{-1}\left[\frac{d_1-d_2}{\sqrt{2}J}\right], \tag{14}$$

where $\mathbf{D}_{AB}=(d_1,d_2,0)$. From Eq. (13) one finds

$$\phi=\frac{1}{2}\tan^{-1}\left[\frac{2t_{xz}}{\sqrt{2}t_{x^2-y^2}}\frac{\lambda}{\varepsilon_{xz}}\right]\approx\left[\frac{\alpha\theta}{\sqrt{2}}\frac{\lambda}{\varepsilon_{xz}}\right], \tag{15}$$

where θ is the angle of tilt of the octahedra, which is 0.05 rad.[12] The spin-orbit coupling constant for a free Cu^{2+} ion is ≤ 0.1 eV (Ref. 13), and ε_{xz} is of the order of 1 eV (Ref. 14) so that the dimensionless spin-orbit coupling constant is ≤ 0.1. This agrees with Moriya's estimate[2] for the fractional change in the Landé g factor.[15] The geometrical factor reduces the magnitude of ϕ further, and one finds $\phi\approx 10^{-3}$. This is in agreement with estimates based on experiment.[3,16].

III. DETERMINATION OF THE FORM OF THE $\mathbf{D}_{ij}$ TERMS FOR DIFFERENT CUPRATES

In this section we show how subtle differences in structure associated with different cuprates lead to very different forms for the Dzyaloshinskii-Moriya interaction and to different magnetic ground states. The form $\mathbf{D}_{ij}$ is determined by requiring that the energy of any configuration of spins is invariant under the symmetry transformations of the crystal structure.

A. La_2CuO_4

In this case the symmetries of interest are those of the CuO planes and the adjacent oxygen atoms. The CuO planes and the apical sites are illustrated for the low-temperature orthorhombic (LTO) and the low-temperature tetragonal (LTT) phases of La_2CuO_4 and its alloys in Figs. 1 and 2, respectively. The $\mathbf{D}_{ij}$ is determined by the symmetries of the two phases and, one finds the pattern of $\mathbf{D}_{ij}$ for the LTO phase shown in Fig. 3(a), as previously shown by Coffey, Bedell, and Trugman,[8] and for the LTT phase shown in Fig. 3(b). The d_i are constants, which are not determined from symmetry. In Sec. II these constants were determined for the LTO phase. A similar analysis has been carried out for the LTT phase, and we find

$$d_3=\frac{-8\lambda t_0^3}{\varepsilon_p^2}\left[\frac{1}{\varepsilon_p}+\frac{1}{U}\right]\left[\frac{\sqrt{3}\alpha\theta t_{r^2-3z^2}}{\varepsilon_{r^2-3z^2}}-\frac{t_{xz}}{\varepsilon_{xz}}\right]$$

and (16)

$$d_4=\frac{-8\lambda t_0^3}{\varepsilon_p^2}\left[\frac{1}{\varepsilon_p}+\frac{1}{U}\right]\left[\frac{\sqrt{3}\alpha\theta t_{r^2-3z^2}}{\varepsilon_{r^2-3z^2}}\right].$$

The magnetic ground state is given by the Hamiltonian

$$H=\sum_{\langle ij\rangle}\left[J\mathbf{S}_i\cdot\mathbf{S}_j+\mathbf{D}_{ij}\cdot(\mathbf{S}_i\times\mathbf{S}_j)\right]. \tag{17}$$

For the LTO phase the ground state is ferromagnetic with two sublattices where the spins lie in a plane defined

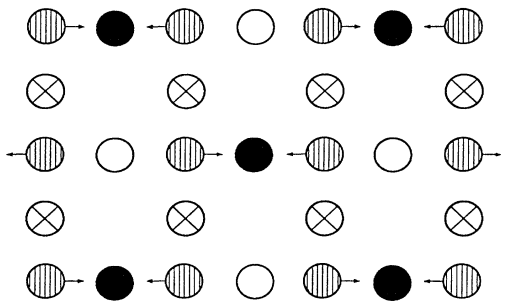

FIG. 2. A CuO_2 plane in the low-temperature tetragonal La_2CuO_4 structure. The symbols are as in Fig. 1 except for the new type of oxygen position, represented by a circle with an $\times$, which remains in the Cu plane. Here the CuO octahedra tilt along the x axis.

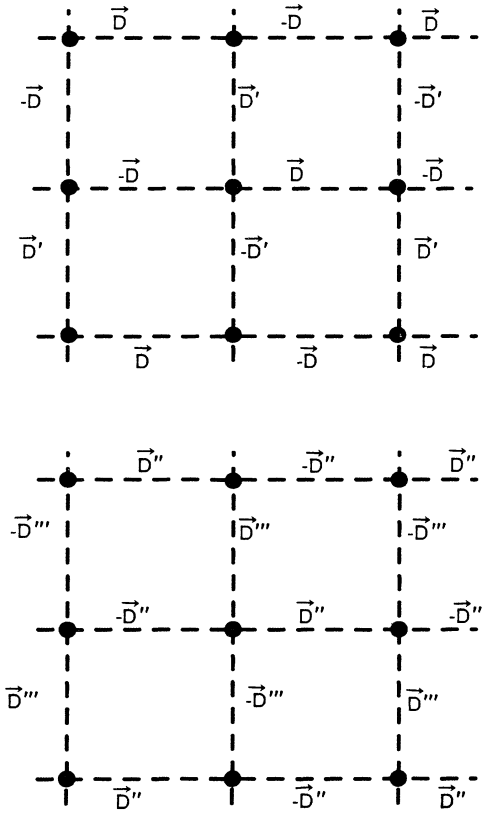

FIG. 3. Pattern of $\mathbf{D}_{ij}$ for the CuO_2 planes in La_2CuO_4 for (a) the low-temperature orthorhombic phase (LTO) and the (b) the low-temperature tetragonal phase (LTT). In the LTO phase $\mathbf{D}=(d_1,d_2,0)$ and $\mathbf{D}'=(-d_2,-d_1,0)$. In the LTT phase $\mathbf{D}''=(0,d_3,0)$ and $\mathbf{D}'''=(0,d_4,0)$.

by the (1,1,0) and the z direction unless $2d_1d_2 > J^2$, which requires that d_1 and d_2 have the same sign. The net ferromagnetic moment per Cu site is $\propto |d_1 - d_2|/J$ and can point in any direction in this plane. For $2d_1d_2 > J^2$ the spins lie in a plane defined by the $(1,-1,0)$ and z directions. In this case pairs of neighboring spins are canted away from antiferromagnetic alignment and the angle is the same for each pair of spins. So the spins spiral in the ground state, and there is no ferromagnetic moment. Given that $|\mathbf{D}_{ij}| \ll J$ in the cuprates, the form of the Dzyaloshinskii-Moriya interaction accounts for the weak ferromagnetism seen experimentally.[3,16]

In the LTT phase the CuO octahedra tilt along mutually perpendicular directions so the spins lie alternatively along the **x** and **y** directions, and the spins lie in a plane defined by the direction in which the CuO octahedra are tilted and the z direction as they do in the LTO phase. There are two kinds of ground state: one with a net moment per CuO plane and one without. In the ground state without a net moment one finds chains of spins in which there is a DM interaction, but which are antiferromagnetically aligned so that there is no moment and the ground-state energy per Cu atom, E_g, is $-0.25[J+(J^2+d^2)^{1/2}]$. In the ground state where there is a net moment per CuO plane each pair of spins is canted from antiferromagnetic order by angle ϕ, which alternates in sign from bond to bond. The magnitude of ϕ and E_g are

$$\phi = \tan^{-1}\left[\frac{d_3+d_4}{2J}\right]$$

and (18)

$$E_g = -\frac{1}{2}\left[J^2+\left[\frac{d_3+d_4}{2}\right]^2\right]^{1/2}.$$

If $(d_3+d_4)^2 > 2d_3^2$, where $|d_3| = \max(|d_3|,|d_4|)$, then the ferromagnetic ground-state energy is lowest. The different forms for the $\mathbf{D}_{ij}$ and the resulting different ground states for the LTO and LTT phases arise from the small difference in crystal structure of the two phases.

As discussed in the Introduction, T_c drops very rapidly in $La_{2-y}Ba_yCuO_4$ for $y = 0.12$, when there is structural transition from the LTO phase to the LTT phase, and recovers when there is a second structural phase transition back to the LTO phase. It is hard to see how such subtle structural changes can lead to sufficiently drastic changes in the phonon spectrum to account for the change in T_c on the basis of the electron-phonon mechanism alone. However, it is not clear whether the different superconductivity and magnetic properties of the LTO and LTT phases are related. Our analysis ignores the effect of holes in the CuO plane without which there is no superconductivity, and it is not known how important the Dzyaloshinskii-Moriya interaction is in an itinerant system or how it would affect superconductivity.

B. $YBa_2Cu_3O_6$

A similar analysis may be carried out for this structure, which is magnetically ordered from temperatures below

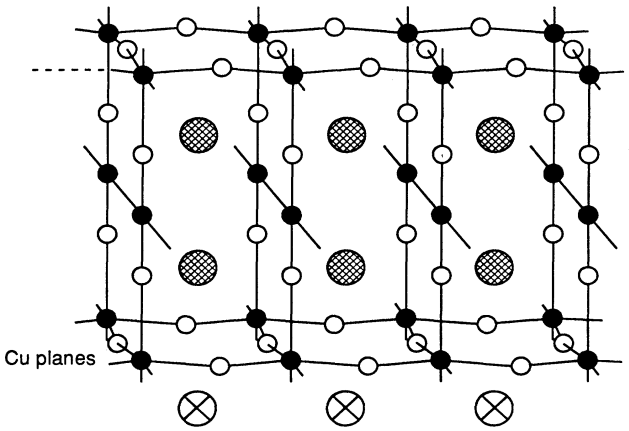

FIG. 4. Structure of $YBa_2Cu_3O_6$. The small solid circles are Cu atoms, the small open circles are oxygen atoms, the large hatched circles are Ba atoms, and the large circles with an $\times$ are yttrium atoms.

≈ 450 K. The structure is shown in Fig. 4. There is a DM interaction between neighboring spins, only for spins in the Cu(2) planes. Unlike the case of the Cu planes in La_2CuO_4, the Cu sites are not centers of inversion, since the adjacent oxygen atoms pop out of the Cu(2) plane in the same direction. Consequently $\mathbf{D}_{ij}$ does not alternate in sign from bond to bond, and there is no ferromagnetic moment in the ground state. The pattern of $\mathbf{D}_{ij}$ for the Cu(2) planes is shown in Fig. 5, and the magnetic ground state has a spiral structure. In the orthorhombic superconducting phase, $YB_2Cu_3O_7$, the pattern of $\mathbf{D}_{ij}$ is the same except that the magnitude may be different along the two bond directions. For this oxygen doping there is no long-range magnetic order, and the possible relevance of $\mathbf{D}_{ij}$ for superconductivity remains obscure.

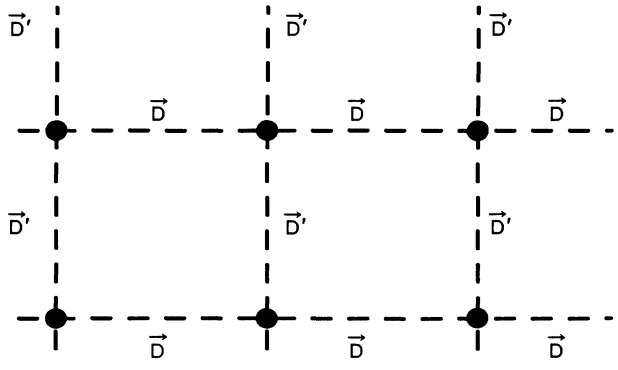

FIG. 5. Pattern of $\mathbf{D}_{ij}$ for CuO_2 planes in $YBa_2Cu_3O_6$. The dots are Cu sites, $\mathbf{D} = (d,0,0,)$ and $\mathbf{D}' = (0,-d,0)$ where d is an unknown constant.

IV. CONCLUSIONS

In this paper we presented microscopic estimates of the DM coupling constants. Due to the small departure of the symmetry from tetragonality and also the weak spin-orbit coupling of the Cu^{2+} ion, these anisotropic coupling constants are small, roughly three orders of magnitude weaker than the isotropic superexchange term. Nonetheless we have seen that such weak terms can have observable consequences for ordered antiferromagnetic structures, e.g., when the DM coupling vectors alternate, a net ferromagnetic moment may be generated.

While the effect of a DM interaction is clear in a state with ordered local moments, it is not clear that the DM interactions would be relevant in superconducting phases. For example, consider the flux phases,[17–21] which have been proposed for the t-J model. In this case the DM-interaction would be a correction to the isotropic t-J Hamiltonian. However, in the flux phase on any Cu-Cu bond the density matrix $(d^{\dagger}_{j\sigma}d_{k\sigma})$ although complex, is diagonal in spin space. The expectation value of the DM interaction, Eq. (11), vanishes in a flux phase, and there is no energy gain of linear order in the $\mathbf{D}_{ij}$ coupling constants. Therefore, there is no obvious stabilization of a flux phase through the DM-interaction. There could possibly be some effect on more general forms, which involve spin rotation.[21]

While the pattern of DM interaction changes upon passing from the orthorhombic to the low-temperature tetragonal phase of the $La_{2-x}Ba_xCuO_4$ family of compounds, it is far from clear how this relates to the change of superconducting T_c associated with this change of crystal structure.

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[1] I. Dzyaloshinskii, J. Phys. Chem. Solids **4**, 241 (1958).
[2] T. Moriya, Phys. Rev. **120**, 91 (1960).
[3] T. Thio *et al.*, Phys. Rev. B **38**, 905 (1988).
[4] For a review of the magnetic structure, see R. J. Birgeneau and G. Shirane, in *Physical Properties of High Temperatures Superconducting,* edited by D. M. Ginsberg (World Scientific, Singapore, 1990).
[5] T. Thio *et al.*, Phys. Rev. B **41**, 231 (1990), see the Appendix.
[6] J. D. Axe, A. H. Moudden, D. Hohlwein, D. E. Cox, K. M. Mahanty, A. R. Moodenbaugh, and Y. Xu, Phys. Rev. Lett. **66**, 2751 (1989).
[7] Y. Maeno, N. Kakehi, A. Odagawa, and T. Fujita, Physica B **165-166**, 1689 (1990).
[8] D. Coffey, K. Bedell, and S. A. Trugman, Phys. Rev. B **42**, 6509 (1990).
[9] P. W. Anderson, Phys. Rev. **115**, 2 (1959).
[10] F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).
[11] D. Coffey, J. Appl. Phys. **69**, 4863 (1991).
[12] S-W. Cheong, J. D. Thompson, and Z. Fisk, Physica C **158**, 109 (1989).
[13] W. Low, in *Solid State Physics Advances in Research and Applications,* edited by F. Seitz and D. Turnbull (Academic, New York, 1960), Vol. 2, p. 77, Table XIX.
[14] A. K. McMahan, R. M. Martin, and S. Satpathy, Phys. Rev. B **38**, 6650 (1988).
[15] S-W. Cheong, J. D. Thompson, and Z. Fisk, Phys. Rev. B **39**, 4395 (1989).
[16] K. K. Singh, P. Ganguly, and J. B. Goodenough, J. Solid State Chem. **52**, 252 (1984).
[17] I. Affleck and J. B. Marston, Phys. Rev. B **37**, 3774 (1988); G. Kotliar, *ibid.* **37**, 3664 (1988).
[18] P. W. Anderson, B. S. Shastry, and D. Hristopoulos, Phys. Rev. B **40**, 8939 (1989).
[19] P. Lederer, D. Poilblanc, and T. M. Rice, Phys. Rev. Lett. **62**, 1519 (1989).
[20] A. B. Harris, T. C. Lubensky, and E. I. Mele, Phys. Rev. B **40**, 2631 (1989).
[21] H. Fukuyama (private communication).