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First-principles investigation of symmetric and antisymmetric exchange interactions of $SrCu_2(BO_3)_2$

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We report on a first-principles investigation of the electronic structure and of the magnetic properties of the quasi-two-dimensional Mott insulator $SrCu_2(BO_3)_2$. Based on the hopping integrals and Coulomb interactions calculated with local-density approximation and local spin density approximation taking into account the on-site Coulomb correlations (LSDA+U), we provide a microscopic explanation of the symmetric Heisenberg and antisymmetric Dzyaloshinskii-Moriya exchange integrals of $SrCu_2(BO_3)_2$. The intra-atomic exchange interaction of oxygen is shown to strongly contribute to the intradimer isotropic exchange. The results are in good agreement with those derived from experimental data, both regarding the orientation of the Dzyaloshinskii-Moriya vectors and the magnitude of all exchange integrals. The microscopic analysis is confirmed by the results of Green's function and total energies difference methods.

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I. INTRODUCTION

The quasi-two-dimensional compound $SrCu_2(BO_3)_2$ has attracted a lot of attention over the past ten years due to its spin-gapped behavior, its finite magnetization below the critical magnetic field deduced from the spin gap, and more importantly its magnetization plateaus at 1/8, 1/4, and 1/3 of the saturated magnetization.[1–3] Based on the quasi-two-dimensional structure of the compound and on a number of experimental facts, the Hamiltonian expected to provide an accurate description of the magnetic properties of that compound must include both Heisenberg symmetric exchange processes and antisymmetric Dzyaloshinskii-Moriya (DM) interactions. It is defined by

$$H = J\sum_{n.n}\vec{S}_i\vec{S}_j + J'\sum_{n.n.n}\vec{S}_i\vec{S}_j + \vec{D}\sum_{n.n}[\vec{S}_i\times\vec{S}_j] + \vec{D}'\sum_{n.n.n}[\vec{S}_i\times\vec{S}_j], \qquad (1)$$

where $J(\vec{D})$ and $J'(\vec{D}')$ define intradimer and interdimer symmetric (Dzyaloshinskii-Moriya) exchange interactions. The Heisenberg model obtained when $\vec{D}$ and $\vec{D}'$ are set to zero is known as the Shastry-Sutherland model.[4] The susceptibility and the main features of the magnetization curve have been interpreted in the context of this Shastry-Sutherland model, leading to estimates of J and J', while the dispersion of triplet excitations, the low-field uniform and staggered magnetizations, and electron spin resonance (ESR) measurements have provided estimates of the DM interactions. A very useful complementary source of information is usually given by first-principles calculations, which have provided valuable results even in low-dimensional quantum spin systems with complex structures.[5,6]

In this paper, we report on a first-principles investigation of the electronic structure and magnetic properties of $SrCu_2(BO_3)_2$. Our results show that an accurate treatment of the oxygen magnetization is crucial for the description of isotropic exchange interactions in $SrCu_2(BO_3)_2$. In order to calculate the DM interactions between magnetic moments, we have used the microscopic expression derived by Moriya.[7] For that purpose, the hopping integrals between different Wannier orbitals centered at Cu atoms have been obtained using a projection procedure. Let us note that the first *ab initio* study of the electronic structure of $SrCu_2(BO_3)_2$ has been performed by J. Liu *et al.*[8] in which the authors calculated the local-density-approximation (LDA) band structure and performed a tight-binding fit to determine the magnitude of the hopping parameters between first- and second-neighbor copper atoms. The analysis reported in the present paper is very different in scope. In particular, it relies on a downfolding of the band structure where all Cu orbitals are taken into account, a crucial ingredient to determine the DM interactions.

The paper is organized as follows: in Sec. II, we shortly describe the crystal structure of $SrCu_2(BO_3)_2$ and present the results of LDA calculations. Sections III and IV contain the analysis of the isotropic and anisotropic exchange interactions. The results of LSDA+U calculations are presented in Sec. V. We discuss and briefly summarize our results in Secs. VI and VII.

II. RESULTS OF LDA CALCULATIONS

The simplified crystal structure of $SrCu_2(BO_3)_2$ is presented in Fig. 1. Each copper atom has one nearest-neighbor Cu atom and four next-nearest-neighbor Cu atoms in $CuBO_3$ layers. In Sr layers, the distance between Cu^{2+} ions is shorter than in $CuBO_3$ layers. However, our results demonstrate, as we will show below, that the magnetic interactions inside the $CuBO_3$ layers are much stronger than in the Sr layers.

The electronic structure calculation of $SrCu_2(BO_3)_2$ has been performed using the tight-binding linear-muffin-tin-orbital atomic sphere approximation (TB-LMTO-ASA) method in terms of the conventional local-density

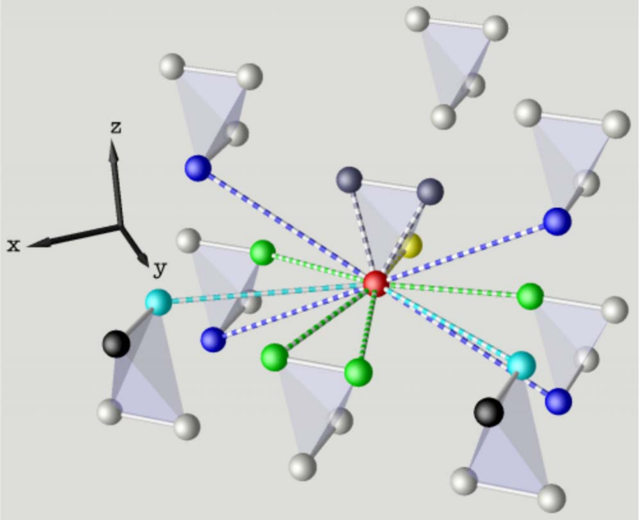


FIG. 1. (Color online) Simplified three-dimensional structure of $SrCu_2(BO_3)_2$. The cycles are copper atoms. The dashed lines correspond to interdimer interaction paths.

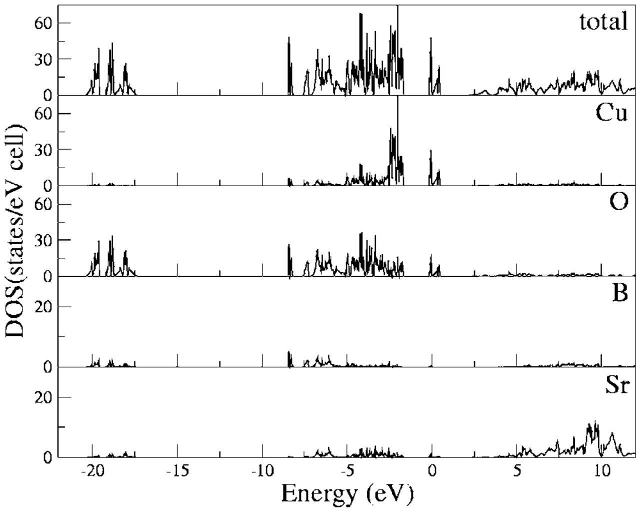


FIG. 2. Total and partial density of states of $SrCu_2(BO_3)_2$ obtained in LDA calculations.

approximation.[9] We used the known crystal structure data.[10] The radii of atomic spheres have been set to $r(\mathrm{Cu})=2.2$ a.u., $r(\mathrm{O})=1.65$ a.u., $r(\mathrm{B})=1.3$ a.u., and $r(\mathrm{Sr})=3.5$ a.u., and nine types of empty spheres were added.

Figure 2 gives the total and partial densities of states projected on the constitutional atoms of the $SrCu_2(BO_3)_2$. The following characteristics can be seen from Fig. 2. (1) The bands lower than -15 eV mostly consist of $2s$ orbitals of the oxygen atoms of the $(BO_3)^{3-}$ complex. (2) The density of states near Fermi level comes mainly from Cu and O orbitals. The band structure of $SrCu_2(BO_3)_2$ near the Fermi level obtained by LDA calculation is presented in Fig. 3. There are four well-separated bands. The analysis of the partial density of states (Fig. 4) shows that the main contribution to these bands comes from copper orbitals with x^2-y^2 symmetry. There is however a contribution of oxygen $2p$ states due to the strong hybridization of Cu $3d$ and O $2p$ states (see Figs. 2 and 4). In this situation, the most natural and simplest way to describe the magnetism and to take into account the hybridization between copper and oxygen is to work in a Wannier function basis.[11,12] We have defined the Wannier functions centered on the copper orbitals with x^2-y^2 symmetry using a projection procedure.[13] The resulting orbitals (presented in Fig. 5) have a strong contribution from the oxygen atomic wave orbitals and can be expressed through the following linear combination:

$$W_i(x) = \alpha\phi_{d_{x^2-y^2}} + 2\beta(\phi_{p_x} + \phi_{p_y}), \tag{2}$$

where α and β are the amplitudes of the copper and oxygen atomic wave functions in the Wannier orbital $W_i(x)$.

III. ISOTROPIC EXCHANGE INTERACTIONS

The results of Sec. II demonstrate that within LDA the $SrCu_2(BO_3)_2$ has a metallic ground state. This is a standard LDA problem for transition-metal oxides, and in order to overcome it one should take into account on-site correlations in the electronic density functional. Despite this problem, a

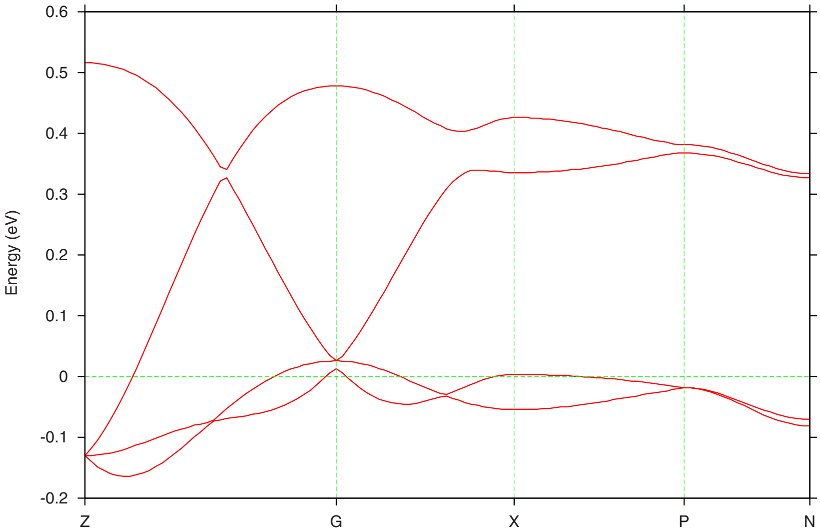


FIG. 3. (Color online) Band structure of $SrCu_2(BO_3)_2$ near Fermi level (0 eV).

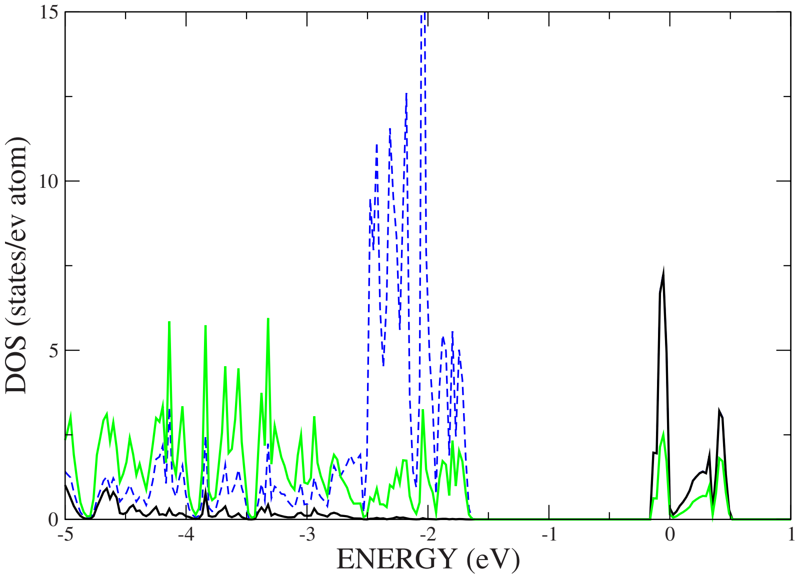


FIG. 4. (Color online) Partial density of $3d$ copper states obtained by LDA calculations. The blue dashed, black, and green solid lines are $3d$ states of copper, $3d_{x^2-y^2}$ orbital, and $2p$ states of oxygen, respectively. The zero energy corresponds to the Fermi level.

microscopic description of magnetic couplings is still possible on the basis of LDA. In order to demonstrate this, we construct a model Hamiltonian describing $SrCu_2(BO_3)_2$ in the Wannier function basis. This Hamiltonian is set to reproduce only four bands of the full Hamiltonian near the Fermi level (Fig. 3). We express the LDA structure results in terms of a low-energy few-orbital model Hamiltonian using a projection procedure.[13] Let us first consider the one-orbital tight-binding Hamiltonian in the Wannier functions basis $H_{TB}=-\Sigma_{i,j,\sigma}t_{ij}^{x^2-y^2}a_{i\sigma}^{+}a_{j\sigma}$, where $t_{ij}^{x^2-y^2}$ is the hopping integral between Wannier functions centered on the $3d_{x^2-y^2}$ orbitals of ith and jth sites. To simplify the analysis we divide the calculated hopping integrals into two subgroups: intraplane (Fig. 6) and interplane (Fig. 7) couplings. The intraplane transfers are $t_{12}^{x^2-y^2}=169$ meV, $t_{13}^{x^2-y^2}=t_{14}^{x^2-y^2}=t_{15}^{x^2-y^2}=t_{16}^{x^2-y^2}=63$ meV, $t_{17}^{x^2-y^2}=t_{18}^{x^2-y^2}=15$ meV, and $t_{19}^{x^2-y^2}=t_{110}^{x^2-y^2}=t_{111}^{x^2-y^2}=t_{112}^{x^2-y^2}=12$ meV. In turn the interplane hopping integrals have the values $t_{1A}^{x^2-y^2}=t_{1B}^{x^2-y^2}=8$ meV and $t_{1C}^{x^2-y^2}=t_{1D}^{x^2-y^2}=t_{1F}^{x^2-y^2}=t_{1E}^{x^2-y^2}=12$ meV.

Using these hopping parameters, one can estimate the magnetic couplings of $SrCu_2(BO_3)_2$. Since the Wannier orbitals have a strong contribution from the wave functions of the oxygen atoms, it is not enough to use the simple formula $\frac{4t_{ij}^2}{U}$. There is an additional ferromagnetic contribution originating from Hund's rule intra-atomic exchange interaction of the oxygen,[5] which leads to the formula

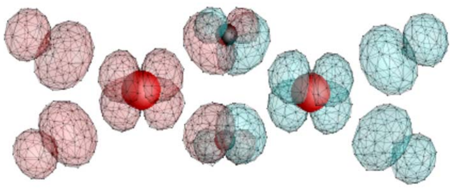


FIG. 5. (Color online) Wannier orbitals centered at x^2-y^2 orbitals of copper atoms which belong to the dimer.

$$J=\frac{4t_{ij}^2}{\alpha^4 U_d}-2\beta^4 J_p^H N_{\text{ox}}, \tag{3}$$

where N_{ox} is the number of oxygen atoms between coppers and β is the contribution of atomic wave functions of oxygen to the Wannier orbitals. U_d and J_p^H are effective on-site Coulomb interaction of copper atom and intra-atomic exchange interaction of oxygen, respectively. The former interaction can be estimated as $U_d=\tilde{U}_d-\tilde{J}_d^H=8.4$ eV, where the on-site Coulomb $\tilde{U}_d$ and intra-atomic exchange interaction $\tilde{J}_d^H$ parameters of copper atom are determined from first-principles constrained LDA calculations: $\tilde{U}_d=9.4$ eV and $\tilde{J}_d^H=1$ eV. According to spin-polarized LSDA+U calculations[5] $J_p^H=1.6$ eV. The value of the copper magnetic moment obtained by LSDA+U calculations is $0.72\mu_B$. One can estimate β^2 through the magnetic moment of the oxygen atom in the ferromagnetic configuration simulated in LSDA+U calculations (Table III): $\beta^2=\text{M(O)}/2=0.05$. Using Eq. (3) and the

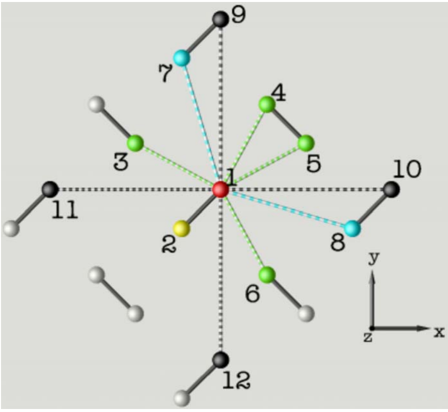


FIG. 6. (Color online) Representation of couplings between atom 1 and its neighbors which belong to the plane. The interactions between atom 1 and the light gray sites without numbers are negligibly small.

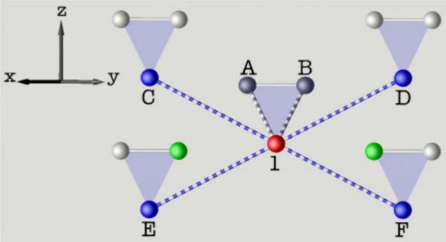


FIG. 7. (Color online) Interplane interactions between copper atoms. The interactions between atom 1 and the light gray sites without letters are negligibly small.

parameters defined above leads to $J_{12}=10.2$ meV. The value of J_{12} is larger than that derived from experimental data. The problem might be that Eq. (3) is sensitive to the form of the Wannier functions. For instance, if β^2 was equal to 0.054 (instead of 0.05), then J_{12} would be equal to 7.5 meV, in excellent agreement with the experimental value. A detailed comparison of our results for the magnetic couplings with those extracted from experiments is presented in Sec. VI.

On the other hand, there is no overlap at oxygen atom between Wannier functions which belong to different dimers, and therefore, the interdimer interactions can be calculated using the standard expression

$$J_{ij}=\frac{4t_{ij}^2}{\alpha^4 U_d}. \tag{4}$$

This leads to $J_{13}=3.6$ meV, $J_{17}=0.2$ meV, $J_{19}=0.13$ meV, $J_{1A}=0.06$ meV, and $J_{1C}=0.13$ meV.

IV. ANISOTROPIC EXCHANGE INTERACTIONS

In a pioneer investigation, Moriya[7] pointed out two main contributions to the anisotropic exchange interaction. The first one is the kinetic Dzyaloshinskii-Moriya interaction, which can be expressed in the following form:

$$\vec{D}_{ij}^{\text{kin}}=\frac{8i}{\alpha^4 U_d}[t_{ij}^{nn'}\vec{C}_{ji}^{n'n}-\vec{C}_{ij}^{nn'}t_{ji}^{n'n}], \tag{5}$$

where n and n' denote the ground-state Wannier orbitals centered at the ith and jth sites, while $t_{ij}^{nn'}$ and $\vec{C}_{ij}^{nn'}$ are transfer integrals without and with spin-orbit coupling. In the case of $SrCu_2(BO_3)_2$, the ground-state Wannier function is centered on the $3d_{x^2-y^2}$ orbital of copper. If the energy difference between the ground state and the excited states is larger than the spin-orbit coupling, then we can treat the spin-orbit interaction as a perturbation. In this case $\vec{C}_{ji}^{n'n}$ is given by

$$\vec{C}_{ji}^{n'n}=-\frac{\lambda}{2}\left(\sum_{m'}\frac{\vec{l}_j^{m'n'*}}{\epsilon_j^{m'}-\epsilon_j^{n'}}t_{ji}^{m'n}+\sum_{m}\frac{\vec{l}_i^{mn}}{\epsilon_i^{m}-\epsilon_i^{n}}t_{ji}^{n'm}\right), \tag{6}$$

where λ is the spin-orbit coupling constant, $\vec{l}_i^{mn}$ is the matrix element of the orbital angular momentum between the mth excited state and the nth ground-state Wannier functions which are centered at ith ion, while ϵ_i^n represents the energy of the nth Wannier orbital at the ith ion.

TABLE I. The energies ϵ_m of the Wannier orbitals obtained using the projection procedure (in eV). The zero energy corresponds to the Wannier orbitals of $3z^2-r^2$ symmetry.

xy	yz	$3z^2-r^2$	zx	x^2-y^2
0.26	0.20	0	0.20	2.54

The second contribution to anisotropic exchange interactions is of Coulomb interaction origin[7] and is given by

$$\vec{D}_{ij}^{\text{Coulomb}}=4i\lambda\left(\sum_{m}\frac{\vec{l}_i^{mn}}{\epsilon_i^{m}-\epsilon_i^{n}}J_{ij}^{nn'n'm}-\sum_{m'}\frac{\vec{l}_j^{m'n'}}{\epsilon_j^{m'}-\epsilon_j^{n'}}J_{ij}^{nn'm'n}\right), \tag{7}$$

where $J_{ij}^{nn'n'm}=\int\int\frac{W_i^{n*}(x)W_j^{n'}(x)W_j^{n'*}(x')W_i^{m}(x')}{|x-x'|}dxdx'$ is a kind of intersite Coulomb exchange interaction, which is nondiagonal with respect to the orbitals. Assuming that the Wannier functions of x^2-y^2 symmetry are ground-state orbitals, these intersite Coulomb exchange interaction integrals can be expressed in the atomic wave-function basis in the following form:

$$\int\int\frac{\phi_{p_y}^*(x)\phi_{p_x}(x)\phi_{p_x}^*(x')\phi_{p_z}(x')}{|x-x'|}dxdx' \tag{8}$$

and

$$\int\int\frac{\phi_{p_x}^*(x)\phi_{p_z}(x)\phi_{p_y}^*(x')\phi_{p_x}(x')}{|x-x'|}dxdx'. \tag{9}$$

One can estimate these integrals through complex spherical harmonics and Slater integrals.[14] We found that, due to symmetry, both integrals of Eqs. (8) and (9) are identically zero. Therefore, we only consider the kinetic Dzyaloshinskii-Moriya interaction in the following.

To perform the microscopic analysis and calculate the kinetic Dzyaloshinskii-Moriya interactions, we define the hopping parameters of the following general tight-binding Hamiltonian that includes five Wannier orbitals centered at Cu sites,

$$H_{\text{TB}}^{5\text{ orb}}=\sum_{\substack{i,j,\sigma\\k,k'}}t_{ij}^{kk'}a_{ik\sigma}^{+}a_{jk'\sigma}, \tag{10}$$

where k, $k'=xy$, yz, $3z^2-r^2$, xz, and x^2-y^2. Using the projection procedure[13] we have calculated the hopping integrals between the ground-state Wannier orbitals of x^2-y^2 symmetry $t_{12}^{x^2-y^2}=161$ meV, $t_{13}^{x^2-y^2}=t_{14}^{x^2-y^2}=t_{15}^{x^2-y^2}=t_{16}^{x^2-y^2}=62$ meV, $t_{17}^{x^2-y^2}=t_{18}^{x^2-y^2}=16$ meV, $t_{19}^{x^2-y^2}=t_{110}^{x^2-y^2}=t_{111}^{x^2-y^2}=t_{112}^{x^2-y^2}=13$ meV, $t_{1A}^{x^2-y^2}=t_{1B}^{x^2-y^2}=12$ meV, and $t_{1C}^{x^2-y^2}=t_{1D}^{x^2-y^2}=t_{1F}^{x^2-y^2}=t_{1E}^{x^2-y^2}=10$ meV. The hopping integrals between the ground state (x^2-y^2) and excited (xy, yz, $3z^2-r^2$, and xz) states Wannier orbitals are given,

$$t_{12}^{yzx^2-y^2} = -t_{12}^{x^2-y^2yz} = -t_{12}^{xzx^2-y^2} = t_{12}^{x^2-y^2xz} = -t_{21}^{yzx^2-y^2} = t_{21}^{x^2-y^2yz} = t_{21}^{xzx^2-y^2} = -t_{21}^{x^2-y^2xz} = 10 \text{ meV}$$

and

$$t_{13}^{x^2-y^2xy} = t_{31}^{xyx^2-y^2} = t_{14}^{xyx^2-y^2} = t_{41}^{x^2-y^2xy} = -t_{15}^{xyx^2-y^2} = -t_{51}^{x^2-y^2xy} = -t_{16}^{x^2-y^2xy} = -t_{61}^{xyx^2-y^2} = -22 \text{ meV},$$

$$t_{13}^{xyx^2-y^2} = t_{31}^{x^2-y^2xy} = t_{14}^{x^2-y^2xy} = t_{41}^{xyx^2-y^2} = -t_{15}^{x^2-y^2xy} = -t_{51}^{xyx^2-y^2} = -t_{16}^{xyx^2-y^2} = -t_{61}^{x^2-y^2xy} = -12 \text{ meV},$$

$$t_{13}^{x^2-y^2xz} = t_{31}^{xzx^2-y^2} = t_{14}^{yzx^2-y^2} = t_{41}^{x^2-y^2yz} = -t_{15}^{xzx^2-y^2} = -t_{51}^{x^2-y^2xz} = -t_{16}^{x^2-y^2yz} = -t_{61}^{yzx^2-y^2} = 15 \text{ meV},$$

$$t_{13}^{x^2-y^2yz} = t_{31}^{yzx^2-y^2} = -t_{14}^{xzx^2-y^2} = -t_{41}^{x^2-y^2xz} = t_{15}^{yzx^2-y^2} = t_{51}^{x^2-y^2yz} = -t_{16}^{x^2-y^2xz} = -t_{61}^{xzx^2-y^2} = -0.001 \text{ meV},$$

$$t_{13}^{yzx^2-y^2} = t_{31}^{x^2-y^2yz} = -t_{14}^{x^2-y^2xz} = -t_{41}^{xzx^2-y^2} = t_{15}^{x^2-y^2yz} = t_{51}^{yzx^2-y^2} = -t_{16}^{xzx^2-y^2} = -t_{61}^{x^2-y^2xz} = -0.003 \text{ meV}.$$

In contrast to the one-orbital model, the value of the intradimer hopping integral between Wannier orbitals of x^2-y^2 symmetry becomes smaller. This is due to the fact that the hybridization between filled and vacant orbitals is explicitly taken into account in the five-orbital model. We can estimate the isotropic exchange interactions in the case of the five-orbital model using Eq. (3), $J_{12}=7.8$ meV, $J_{13}=3.5$ meV, $J_{17}=0.23$ meV, $J_{19}=0.15$ meV, $J_{1A}=0.13$ meV, and $J_{1C}=0.09$ meV. These values are in better agreement with the experimental estimates.

The energies of the Wannier orbitals obtained by the projection procedure[13] are shown in Table I. Using these hopping integrals, we find that Eq. (5) can be reduced to the following expression for the x and y components of the intradimer Dzyaloshinskii-Moriya interaction ($i=1$ and $j=2$):

$$D_{12}^{x} = \frac{16\lambda}{\alpha^4 U_d(\epsilon_{yz}-\epsilon_{x^2-y^2})} t_{12}^{x^2-y^2} t_{21}^{yzx^2-y^2} \tag{11}$$

and

$$D_{12}^{y} = \frac{16\lambda}{\alpha^4 U_d(\epsilon_{xz}-\epsilon_{x^2-y^2})} t_{12}^{x^2-y^2} t_{21}^{xzx^2-y^2}. \tag{12}$$

The z component of the interdimer ($i=1$ and $j=3,4,5,6$) coupling is given by

$$D_{ij}^{z} = \frac{8\lambda t_{ij}^{x^2-y^2}}{\alpha^4 U_d(\epsilon_{xy}-\epsilon_{x^2-y^2})}\left[t_{ji}^{x^2-y^2xy} - t_{ji}^{xyx^2-y^2} + t_{ij}^{xyx^2-y^2} - t_{ij}^{x^2-y^2xy}\right], \tag{13}$$

and the x and y components of the interdimer interactions are given by

$$D_{13}^{x} = \frac{4\lambda t_{13}^{x^2-y^2}}{\alpha^4 U_d(\epsilon_{yz}-\epsilon_{x^2-y^2})}\left[t_{31}^{yzx^2-y^2} - t_{31}^{x^2-y^2yz} - t_{13}^{yzx^2-y^2} + t_{13}^{x^2-y^2yz}\right], \tag{14}$$

$$D_{13}^{y} = \frac{4\lambda t_{13}^{x^2-y^2}}{\alpha^4 U_d(\epsilon_{xz}-\epsilon_{x^2-y^2})}\left[t_{31}^{xzx^2-y^2} + t_{13}^{x^2-y^2xz}\right], \tag{15}$$

$$D_{14}^{x} = \frac{4\lambda t_{14}^{x^2-y^2}}{\alpha^4 U_d(\epsilon_{yz}-\epsilon_{x^2-y^2})}\left[t_{41}^{x^2-y^2yz} + t_{14}^{yzx^2-y^2}\right], \tag{16}$$

$$D_{14}^{y} = \frac{4\lambda t_{14}^{x^2-y^2}}{\alpha^4 U_d(\epsilon_{xz}-\epsilon_{x^2-y^2})}\left[t_{41}^{xzx^2-y^2} - t_{41}^{x^2-y^2xz} - t_{14}^{xzx^2-y^2} + t_{14}^{x^2-y^2xz}\right], \tag{17}$$

$$D_{15}^{x} = \frac{4\lambda t_{15}^{x^2-y^2}}{\alpha^4 U_d(\epsilon_{yz}-\epsilon_{x^2-y^2})}\left[t_{51}^{yzx^2-y^2} - t_{51}^{x^2-y^2yz} - t_{15}^{yzx^2-y^2} + t_{15}^{x^2-y^2yz}\right], \tag{18}$$

$$D_{15}^{y} = \frac{4\lambda t_{15}^{x^2-y^2}}{\alpha^4 U_d(\epsilon_{xz}-\epsilon_{x^2-y^2})}\left[t_{51}^{x^2-y^2xz} + t_{15}^{xzx^2-y^2}\right], \tag{19}$$

$$D_{16}^{x}=\frac{4\lambda t_{16}^{x^2-y^2}}{\alpha^4 U_d(\epsilon_{yz}-\epsilon_{x^2-y^2})}[t_{61}^{yzx^2-y^2}+t_{16}^{x^2-y^2yz}], \tag{20}$$

and

$$D_{16}^{y}=\frac{4\lambda t_{16}^{x^2-y^2}}{\alpha^4 U_d(\epsilon_{xz}-\epsilon_{x^2-y^2})}[t_{61}^{xzx^2-y^2}-t_{61}^{x^2-y^2xz}-t_{16}^{xzx^2-y^2}+t_{16}^{x^2-y^2xz}]. \tag{21}$$

We are now in a position to calculate Dzyaloshinskii-Moriya interactions using Eqs. (11)–(21) and the value of spin-orbit coupling $\lambda=0.1$ eV. These results are presented in Table II and Fig. 8. In the notation of Eq. (1) $\vec{D}$ and $\vec{D}'$ correspond to $\vec{D}_{12}$ and $\vec{D}_{1j}$ (where $j=3,4,5,6$), respectively. Based on Eqs. (11) and (12), we can conclude that the source of intradimer anisotropic exchange interaction is the hopping process between Wannier orbitals of x^2-y^2 and $yz(xz)$ symmetry. The microscopic origin of the interdimer Dzyaloshinskii-Moriya interaction is the transfer process between x^2-y^2 and xy Wannier orbitals. It is interesting to note that there are x and y components of interdimer anisotropic couplings. The comparison with experimental data is presented in Sec. VI. In Sec. V we present the results of LSDA+U calculations, which give additional confirmation of our model consideration for the isotropic interactions.

V. RESULTS OF LSDA+U CALCULATIONS

The results of LDA calculations have demonstrated that the magnetic properties of $SrCu_2(BO_3)_2$ can be reproduced correctly within the microscopic model approach based on the LDA calculations. However, LDA cannot correctly describe the insulating ground state of $SrCu_2(BO_3)_2$. In order to overcome this problem, we have used the LSDA+U approximation,[15] which takes into account the Coulomb correlations of localized states neglected in LDA. The Coulomb interaction $\tilde{U}_d$ and the intra-atomic exchange $\tilde{J}_d^H$ of the copper atoms, which represent external parameters in a self-consistent cycle of the LSDA+U scheme, are determined from the first-principles calculation by constrained LDA. The calculation scheme has been described elsewhere.[16] The Coulomb interaction parameter $\tilde{U}_d$ and the intra-atomic exchange $\tilde{J}_d^H$ have been estimated to be $\tilde{U}_d=9.4$ eV and $\tilde{J}_d^H=1$ eV.

TABLE II. Calculated anisotropic exchange interaction vectors $\vec{D}_{ij}$ (in meV).

(i,j)	$\vec{D}_{ij}$
(1,2)	(0.25;–0.25;0.0)
(1,3)	(–0.01; –0.07; –0.1)
(1,4)	(–0.07; –0.01; 0.1)
(1,5)	(0.01; 0.07; –0.1)
(1,6)	(0.07;0.01; 0.1)

We have performed LSDA+U calculations for two magnetic configurations, which are presented in Fig. 9. The results of these calculations are presented in Table III. In both cases, $SrCu_2(BO_3)_2$ is an insulator with an energy gap of 2.2 eV. The antiferromagnetic configuration has a lower energy.

Let us describe the interdimer interactions. For that we use the Green's function method. Following Lichtenstein *et al.*,[17] we determine the exchange interaction parameter between copper atoms via the second variation in the total energy with respect to small deviations of the magnetic moments from the collinear magnetic configuration. The exchange interaction parameters J_{ij} can be written in the following form:[17,18]

$$J_{ij}=\frac{2}{\pi}\int_{-\infty}^{E_F}d\epsilon\,\mathrm{Im}\sum_{\substack{m,m'\\ m'',m'''}}(\Delta_i^{mm'}G_{ij\downarrow}^{m'm''}\Delta_j^{m''m'''}G_{ji\uparrow}^{m'''m}),$$

where m is the magnetic quantum number, the on-site potential $\Delta_i^{mm'}=H_{ii\uparrow}^{mm'}-H_{ii\downarrow}^{mm'}$, and the Green's function is calculated in the following way:

$$G_{ij\sigma}^{mm'}(\epsilon)=\sum_{k,n}\frac{c_{i\sigma}^{mn}(k)c_{j\sigma}^{m'n*}(k)}{\epsilon-E_{\sigma}^{n}}. \tag{22}$$

Here $c_{i\sigma}^{mn}$ is a component of the nth eigenstate and E_{σ}^{n} is the corresponding eigenvalue. This leads to the following inter-

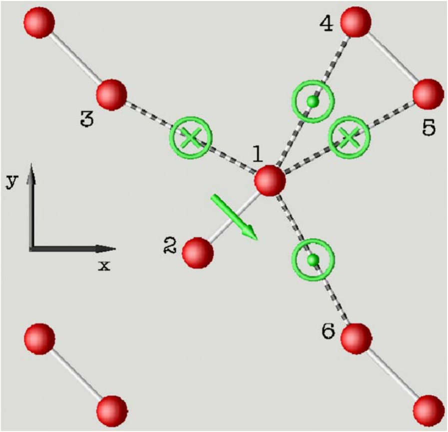
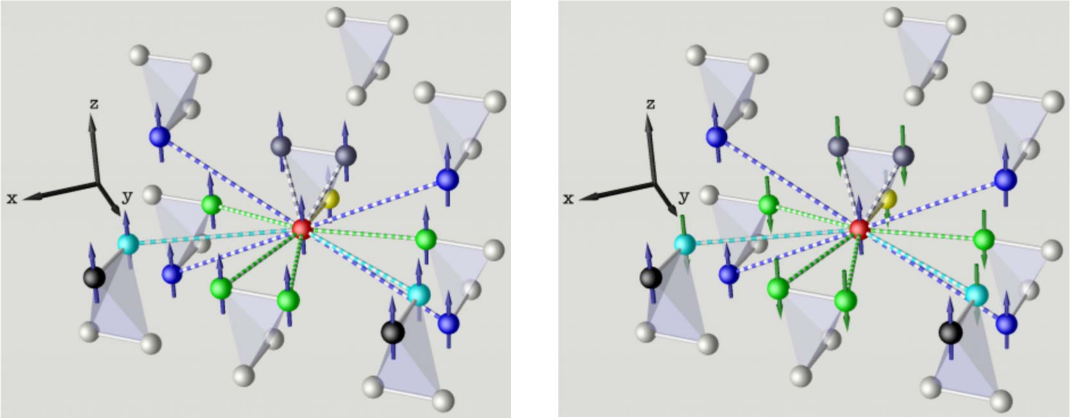


FIG. 8. (Color online) Schematic representation of symmetry of Dzyaloshinskii-Moriya interactions.



(a) (b)

FIG. 9. (Color online) Ferromagnetic and antiferromagnetic configurations simulated in LSDA+U calculations.

dimer exchange interactions: $J_{13}=J_{14}=J_{15}=J_{16}=4.1$ meV, $J_{17}=J_{18}=0.17$ meV, $J_{19}=J_{110}=J_{111}=J_{112}=0.06$ meV, $J_{1A}=J_{1B}=0.06$ meV, and $J_{1C}=J_{1D}=J_{1E}=J_{1F}=0.02$ meV.

One can see that in the case of the antiferromagnetic configuration there is no magnetic moment at the oxygen atom (Table III). But in the ferromagnetic configuration, the oxygen has a small moment. This fact supports the scenario proposed in Ref. 5. Therefore, to calculate the intradimer exchange interaction, it is necessary to take into account the change in oxygen magnetization. One can do this using the method of total energies difference.

For that purpose, we write the Heisenberg Hamiltonian in the following form:

$$H=\sum_{i>j} J_{ij}\vec{S}_i\vec{S}_j. \tag{23}$$

The total energies of the ferromagnetic and antiferromagnetic configurations presented in Fig. 9 are

$$E_{\mathrm{FM}}=J_{12}S^2+4J_{13}S^2+2J_{17}S^2 \tag{24}$$

and

$$E_{\mathrm{AFM}}=-J_{12}S^2-4J_{13}S^2-2J_{17}S^2. \tag{25}$$

Therefore, the dimer exchange interaction J_{12} is given by

TABLE III. Results of LSDA+U calculations for ferromagnetic and antiferromagnetic configurations. E_{gap} is the value of the energy gap (in eV). M(Cu) and M(O) are the values of the magnetic moments of copper and oxygen atoms which are located between the copper atoms in dimer (in μ_B). E_{tot} is the relative total energy of the system in different magnetic configurations (in meV).

	E_{gap}	M(Cu)	M(O)	E_{total}
FM	2.2	0.72	0.1	12
AFM	2.2	0.72	0	0

$$J_{12}=\frac{E_{\mathrm{FM}}-E_{\mathrm{AFM}}-8J_{13}S^2-4J_{17}S^2}{2S^2}. \tag{26}$$

Using calculated values of the interdimer couplings ($J_{13}=4.1$ meV and $J_{17}=0.17$ meV) and the values of the total energies from Table III, one can calculate the dimer exchange interaction for $S=1/2$, which leads to $J_{12}=7.3$ meV.

VI. COMPARISON WITH EXPERIMENT

The exchange interactions obtained with different methods are summarized in Table IV, together with the values most often used to explain experimental data. The Green's function method is in principle the most accurate, and if its results are in good agreement with those obtained by LDA using microscopic exchange formulae, which is the case here, the results are expected to be quite accurate. The agreement with experimental estimates is quite good for J_{12} and J_{13}. The interplane coupling J_{1A} is however predicted to be about ten times smaller than what has been suggested from fitting the susceptibility, a conclusion to be taken seriously in view of the overall good agreement regarding the other parameters. Besides, the dominant couplings beyond J_{12} and J_{13} are predicted to be the in-plane exchange couplings J_{17} and J_{19}, parameters which have not been considered so far in theoretical models of $\mathrm{SrCu_2(BO_3)_2}$.

TABLE IV. Values of exchange interactions J_{ij} between magnetic moments of $\mathrm{SrCu_2(BO_3)_2}$ system (in meV).

	LDA[a]	LDA[b]	LDA+U [c]	Exp. (after Ref. 1)
J_{12}	10.6	7.8	7.3	7.3
J_{13}	3.6	3.5	4.1	4.6
J_{17}	0.2	0.23	0.17	
J_{19}	0.13	0.15	0.06	
J_{1A}	0.06	0.13	0.06	0.66
J_{1C}	0.13	0.09	0.02	

[a] One-orbital model.
[b] Five-orbital model.
[c] Green's function approach.

Let us go beyond these general statements and look in more details at how well the calculated exchange parameters can reproduce basic experimental facts such as the spin gap and the temperature dependences of the magnetic susceptibility and specific heat. Let us start with the spin gap analysis. According to different experiments,[1] the value of the spin gap varies from 2.6 meV (nuclear quadrupole resonance) to 3.1 meV (nuclear magnetic resonance). Based on the calculated exchange interactions (Table IV), if we estimate the spin gap using the following expression:[1]

$$\Delta = J_{12}\left[1 - \left(\frac{J_{13}}{J_{12}}\right)^2 - \frac{1}{2}\left(\frac{J_{13}}{J_{12}}\right)^3 - \frac{1}{8}\left(\frac{J_{13}}{J_{12}}\right)^4\right]. \qquad (27)$$

the spin gap value is 9.1 meV in the case of the one-orbital model. This is about three times larger than experimental value. A better agreement is achieved in the five-orbital model and LSDA+U calculations, $\Delta^{5\mathrm{orb}}=5.8$ meV and $\Delta^{\mathrm{LSDA}+U}=4.2$ meV. Let us note however that $J_{13}/J_{12}\simeq 0.6$ is not that small, and higher-order corrections to the estimate of Eq. (27) are expected to further reduce the gap, hence, to improve the agreement with the experimental determination of the gap.

The results of measurements of magnetic susceptibility and specific heat can be reproduced using the Heisenberg model with different sets of isotropic parameters. For instance, in the review of Miyahara and Ueda,[1] there are five different sets of exchange couplings which vary from $J=6.6$ meV and $J'=4.1$ meV to $J=7.3$ meV and $J'=4.6$ meV. The latter J and J' correspond to the best fitting to the experimental data. These values are in reasonable agreement with our exchange interactions for the five-orbital model ($J_{12}=7.8$ meV and $J_{13}=3.5$ meV) and in good agreement with those obtained by LSDA+U calculations ($J_{12}=7.3$ meV and $J_{13}=4.1$ meV).

Let us now turn to the Dzyaloshinskii-Moriya interactions. The presence of such anisotropic interactions in $\mathrm{SrCu_2(BO_3)_2}$ has been revealed by a careful interpretation of inelastic neutron-scattering experiments,[19] which pointed to a significant interdimer DM interaction, and by ESR (Ref. 20) and nuclear magnetic resonance (NMR),[21] which showed that a significant intradimer DM interaction was also present. The problem of the magnon dispersion has been recently revisited by Cheng *et al.*,[22] including all DM interactions allowed by symmetry. Following Ref. 22, the various DM interactions can be conveniently reexpressed in terms of four parameters: (i) The magnitude of the intradimer DM interaction (which by symmetry has to be perpendicular to the bond) D, (ii) the magnitude of the interdimer interaction along z (perpendicular to the plane) D'_z, (iii) the magnitude of the nonstaggered in-plane interdimer interaction D'_{ns}, and (iv) the magnitude of the staggered in-plane interdimer interaction D'_{s}. These parameters are related to the parameters of Table II by the following relations: $D=(D^x_{12}-D^y_{12})/\sqrt{2}$, $D'_z=D^z_{14}$, $D'_{\mathrm{s}}=-(D^x_{14}+D^y_{14})/\sqrt{2}$, and $D'_{\mathrm{ns}}=(-D^x_{14}+D^y_{14})/\sqrt{2}$. Our *ab initio* investigation leads to the following estimates: $D=0.35$ meV, $D'_z=0.1$ meV, $D'_{\mathrm{s}}=0.06$ meV, and $D'_{\mathrm{ns}}=0.04$ meV. These results are in quite good agreement with the information deduced from various experiments. In particular, the hierarchy $D>D'_z>D'_{\mathrm{s}}, D'_{\mathrm{ns}}$ is recovered. The value for the intradimer interaction $D=0.35$ meV is in quantitative agreement with the estimates deduced from ESR (Ref. 20) and NMR.[21] The interdimer interaction perpendicular to the plane $D'_z=0.1$ meV is smaller than the value deduced from the splitting of the neutron dispersion[19] (0.18 meV), but still of the same order of magnitude. In addition, assuming $J'/J=0.63$,[1] the combination $|D'_{\mathrm{s}}-DJ'/2J|=0.05$ meV (Ref. 23) is in reasonable agreement with the constraint deduced by Cheng *et al.*[22] (0.07 meV). Finally, let us note that the signs of the D'_z interactions agree with that deduced by Kodama *et al.*[21] from the observation that there is an anticrossing at the critical field where the gap should close, as well as with that deduced from the interpretation of far-infrared experiments.[24,25]

VII. CONCLUSION

In this paper we have presented the results of an *ab initio* investigation of the magnetic properties of $\mathrm{SrCu_2(BO_3)_2}$. It is found that the ferromagnetic contribution of the intra-atomic exchange interactions of oxygen plays a crucial role to account for the intradimer isotropic exchange interaction. The microscopic origin of Dzyaloshinskii-Moriya interactions has been analyzed using calculated hopping integrals between different Wannier orbitals of copper atoms. In general, there are two contributions to anisotropic exchange interaction, which are kinetic and Coulomb Dzyaloshinskii-Moriya interactions. In the case of $\mathrm{SrCu_2(BO_3)_2}$ the Coulomb contribution is zero by symmetry. However, we expect that the latter plays important role in the case of more distorted frustrated cuprates such as $\mathrm{Cu_2Te_2O_5(Br,Cl)_2}$ and $\mathrm{(Tl,K)CuCl_3}$.

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