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Absence of a spiral magnetic order in Li_2CuO_2 containing one-dimensional CuO_2 ribbon chains

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On the basis of first-principles density functional theory electronic structure calculations as well as classical spin analysis, we explored why the magnetic oxide Li_2CuO_2, consisting of CuO_2 ribbon chains made up of edge-sharing CuO_4 squares, does not exhibit a spiral-magnetic order. Our work shows that, due to the next-nearest-neighbor interchain interactions, the observed collinear magnetic structure becomes only slightly less stable than the spin-spiral ground state and many states become nearly degenerate in energy with the observed collinear structure. This suggests that the collinear magnetic structure of Li_2CuO_2 is a consequence of order by disorder induced by next-nearest-neighbor interchain interactions.

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Copper oxides with CuO_2 ribbon chains made up of edge-sharing CuO_4 squares have one-dimensional chains of spin-$\frac{1}{2}$ Cu^{2+} ions and exhibit unique physical properties. $LiCu_2O_2$ (Ref. 1) and $LiCuVO_4$ (Ref. 2) show ferroelectricity when their CuO_2 ribbon chains undergo a spiral-magnetic order at low temperatures. For a chain of spin-$\frac{1}{2}$ ions, a spin-spiral structure is predicted when the nearest-neighbor (NN) ferromagnetic (FM) spin exchange J_1 and the next-nearest-neighbor (NNN) antiferromagnetic (AFM) spin exchange J_2 satisfy the condition $|J_2/J_1|>0.25$, while an FM structure is predicted if $|J_2/J_1|<0.25$.[3] The copper oxide Li_2CuO_2 (Refs. 4–6) also consists of CuO_2 ribbon chains, but has a different magnetic structure. A neutron powder diffraction study of Li_2CuO_2 at 1.5 K showed a collinear magnetic structure in which the spins of each CuO_2 chain has an FM arrangement with Cu moments perpendicular to the plane of the CuO_2 ribbon and the arrangement between adjacent FM chains is AFM[7] (hereafter this magnetic structure will be referred to as the AFM-I state). Thus, to explain this collinear magnetic structure, one might expect $|J_2/J_1|<0.25$ for the CuO_2 chains of Li_2CuO_2. Indeed, de Graaf *et al.* obtained $|J_2/J_1|=0.15$ on the basis of first-principles electronic structure calculations using the embedded cluster model.[8] However, the CuO_2 ribbon chains of Li_2CuO_2 are similar in structure to those of $LiCu_2O_2$ and $LiCuVO_4$, so that $|J_2/J_1|>0.25$ would have been expected. If $|J_2/J_1|>0.25$, one needs to ask why a spiral magnetic order does not occur in Li_2CuO_2. In addition, more than two spin exchange interactions are necessary to describe the magnetic structure of Li_2CuO_2, and the nature and magnitude of these interactions are not unequivocal.[9,10] Another puzzle concerning Li_2CuO_2 is that it undergoes a phase transition below ~2.4 K to a state believed to be a spin-canted state.[11–13] So far, the origin and the nature of this phase transition remain unclear.

The spiral magnetic order of $LiCu_2O_2$ and $LiCuVO_4$ is a consequence of the spin frustration associated with the NN FM and NNN AFM interactions in their CuO_2 chains. A collinear magnetic order can occur as a consequence of order by disorder,[14,15] which occurs typically in highly spin-frustrated systems.[16] Provided that a spin-spiral state is the ground state for the CuO_2 chains of Li_2CuO_2, one might speculate if the AFM-I state of Li_2CuO_2 is close in energy to the spin-spiral state and if Li_2CuO_2 has a large number of nearly degenerate states around the AFM-I state. In the present work we explore these possibilities by studying the magnetic structure of Li_2CuO_2 on the basis of first-principles density functional theory (DFT) electronic structure calculations and carrying out a classical spin analysis with the spin-exchange parameters deduced from the DFT calculations.

Our DFT electronic structure calculations employed the full-potential augmented-plane-wave plus local-orbital method as implemented in the WIEN2k code.[17] For the exchange-correlation energy functional, the generalized gradient approximation[18] (GGA) was employed[19] with $R_{MT}^{min}K_{max}=7.0$. To properly describe the strong electron correlation in the $3d$ transition-metal oxide, the GGA plus on-site repulsion U method (GGA+U) was employed.[20] We also examined the energy of Li_2CuO_2 as a function of the magnetic order parameter $\mathbf{q}$ by employing the noncollinear magnetism code WIENncm.[21]

Li_2CuO_2 has a body-centered orthorhombic structure

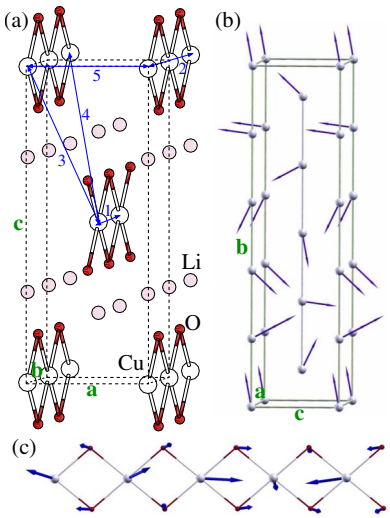

FIG. 1. (Color online) (a) Crystal structure and five spin-exchange paths J_1–J_5 of Li_2CuO_2. (b) Cu moments of the spin spiral ground state at $\mathbf{q}=(0,0.20,0)$ obtained from the GGA+U noncollinear calculation with $U_{eff}=6$ eV. (c) Detailed view of the Cu and O moments of a CuO_2 ribbon chain in the spin-spiral ground state shown in (b). For the purpose of illustration, the O moments were increased by 3 times.

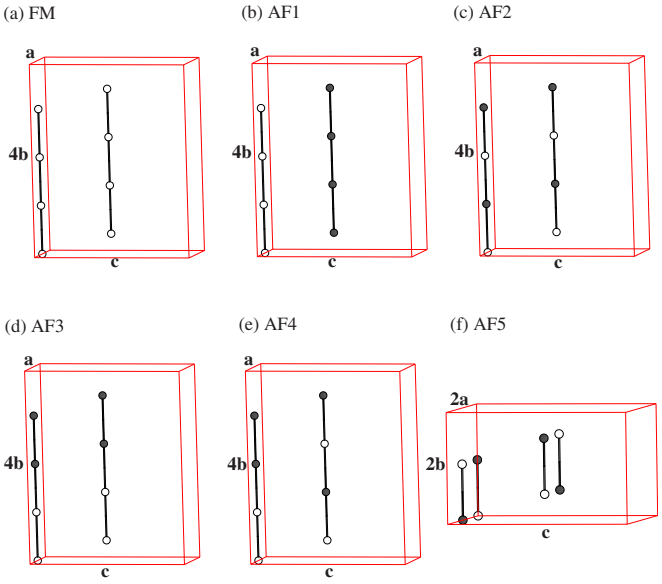

FIG. 2. (Color online) Schematic representations of the six ordered spin arrangements of Li_2CuO_2 employed for GGA+U calculations to extract the five spin-exchange parameters J_1–J_5. The solid and open circles represent the up-spin and down-spin Cu sites, respectively.

(space group *Immm* with a=3.654 Å, b=2.860 Å, and c=9.377 Å),[7] where the CuO_2 ribbon chains run along the b direction (Fig. 1). As depicted in Fig. 1(a), there are five possible spin-exchange interactions to consider; J_1 and J_2 are NN and NNN intrachain interactions, respectively, and J_3 and J_4 are NN and NNN interchain interactions along the c direction, respectively, while J_5 is the interchain interaction along the a direction. To evaluate the interactions J_1–J_5, we calculate the relative energies of the six ordered collinear spin states shown in Fig. 2 in terms of GGA+U calculations. To see the dependence of these spin-exchange interactions on the effective on-site repulsion $U_{eff}=U-J$, our GGA+U calculations were carried out with U_{eff} ranging from 0 to 10 eV. (For 3d transition metals, U is generally less than 10 eV and the J value is usually 1 eV.) The relative energies of the six ordered spin states of Fig. 2 obtained from our GGA+U calculations are summarized in Table I. Table I shows that the lowest-energy state is the AF3 state when $U_{eff} \leqslant 4$ eV, but it is the AF1 state otherwise. In general, the U_{eff} values in the region of 6 eV are most appropriate for Cu-containing

TABLE I. Relative energies per unit cell (in meV) of the various magnetic states with respect to the FM state obtained from GGA+U calculations with different U_{eff} values. There are eight formula units per unit cell (see Fig. 2).

U_{eff} (eV)	0	2	4	6	8	10
E(AF1)	−76.72	−46.40	−30.72	−19.04	−11.68	−7.68
E(AF2)	5.52	39.12	46.08	46.56	37.60	29.36
E(AF3)	−125.12	−64.08	−34.32	−15.68	−5.68	−1.44
E(AF4)	−53.28	−8.00	9.84	17.84	17.76	15.04
E(AF5)	10.00	40.00	46.16	46.40	37.20	29.20

TABLE II. Calculated exchange parameters (in meV) deduced from GGA+U calculations.

U_{eff} (eV)	0	2	4	6	8	10
J_1	−10.98	−15.58	−15.36	−14.02	−10.86	−8.31
J_2	23.91	15.78	10.44	7.35	4.48	3.00
J_3	1.07	0.34	−0.04	−0.01	−0.09	−0.03
J_4	3.73	2.56	1.95	1.20	0.82	0.51
J_5	−1.12	−0.22	−0.01	0.05	0.09	0.05

magnetic oxides. In terms of the exchange parameters J_1–J_5, the energies of the six magnetic states per Cu are written as

$$E(FM) = (J_1 + J_2 + 4J_3 + 4J_4 + J_5)/4,$$

$$E(AF1) = (J_1 + J_2 - 4J_3 - 4J_4 + J_5)/4,$$

$$E(AF2) = (-J_1 + J_2 + J_5)/4,$$

$$E(AF3) = (-J_2 + 2J_3 - 2J_4 + J_5)/4,$$

$$E(AF4) = (-J_1 + J_5)/8,$$

$$E(AF5) = (-J_1 + J_2 - J_5)/8. \quad (1)$$

Thus, by equating the energy differences of these states in terms of the spin-exchange parameters with the corresponding energy differences in terms of the GGA+U calculations, we obtain the values of J_1–J_5 summarized in Table II, where we employed the convention in which positive and negative numbers represent AFM and FM interactions, respectively. J_5 is very weak in agreement with Mizuno *et al.*[10] The NNN interchain interaction J_4 is much stronger than the NN interchain interaction J_3, and this finding does not support the assumption by Mizuno *et al.* that J_3 and J_4 are similar.[10] J_4 is stronger than J_3 because the overlap between the magnetic orbitals, which depends on the overlap between the O 2p orbitals of the magnetic orbitals,[22] is much more favorable for the path J_4 than for the path J_3 (Fig. 3). The NN intrachain interaction J_1 is FM while the NNNintrachain interac-

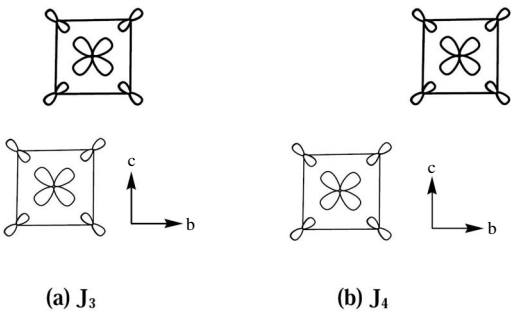

FIG. 3. Arrangements of the CuO_4 squares and their magnetic orbitals associated with (a) the NN interchain interaction J_3 and (b) the NNN interchain interaction J_4. The two adjacent CuO_2 ribbon chains differ in their a-axis heights by a/2. The CuO_4 squares with different a-axis heights are indicated by thick and thin lines.

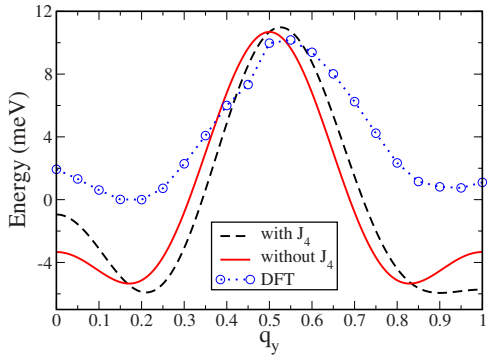

FIG. 4. (Color online) $E(0,q_y,0)$ vs $(0,q_y,0)$ relations calculated for Li_2CuO_2. The solid and dashed lines are based on the classical spin analysis (solid line, only with the intrachain interactions J_1 and J_2; dashed line, with the intrachain interactions J_1 and J_2 as well as the interchain interaction J_4). The dotted line is based on noncollinear GGA+U calculations with U_{eff}=6 eV, where the circles represent the calculated points.

tion J_2 is AFM. These intrachain interactions are the same in nature to those reported by de Graaf *et al.*[8] However, our study shows that $|J_2/J_1|>0.25$, for all U_{eff} values employed, and hence Li_2CuO_2 should have a spin-spiral ground state as far as isolated CuO_2 ribbon chains are concerned.

To see how the above prediction is affected by the NNN interchain interaction J_4, we carried out a classical spin analysis based on the Freiser method[23,24] using the three dominant exchange parameters J_1, J_2, and J_4. The spin interaction energy of an ordered spin state with $\mathbf{q}=(2\pi q_x/a, 2\pi q_y/b, 2\pi q_z/c)$ can be written as

$$E(\mathbf{q}) = J_4\{\cos[2\pi(q_x/2+3q_y/2+q_z/2)]+\cos[2\pi(-q_x/2+3q_y/2+q_z/2)]+\cos[2\pi(q_x/2-3q_y/2+q_z/2)]+\cos[2\pi(q_x/2+3q_y/2-q_z/2)]\}+\cos(2\pi q_y)J_1+\cos(4\pi q_y)J_2. \quad (2)$$

For simplicity of our discussion, we will represent $\mathbf{q}$ by (q_x, q_y, q_z). This $E(\mathbf{q})$ vs $\mathbf{q}$ relation has minima along the $(0,q_y,0)$ direction. The $E(0,q_y,0)$ vs $(0,q_y,0)$ curves calculated with the spin-exchange parameters derived from the GGA+U calculations for U_{eff}=6 eV are presented in Fig. 4. The solid curve, obtained only with the intrachain interactions J_1 and J_2, shows two minima (at q_y=0.18 and q_y=0.82) of equal energy. The FM state (q_y=0.00) and the AFM-I state (q_y=1.00) are identical in energy and are less stable than the two spin-spiral states (q_y=0.18 and q_y=0.82). These are the expected results in the absence of the interchain interaction because $|J_2/J_1|>0.25$. The dashed curve, obtained with the intrachain interactions J_1 and J_2 as well as the interchain interaction J_4, also shows two minima at q_y=0.21 and q_y=0.90. Note that the interchain interaction J_4 raises the energy of the FM state while lowering that of the AFM-I state. As a result, the $E(0,q_y,0)$ vs $(0,q_y,0)$ curve around q_y=0.21 becomes sharper while that around q_y=0.90–1.00 is nearly flat. Both spin-spiral states are only slightly more stable than the collinear AFM-I state. Our calculations using the spin-exchange parameters obtained with $U_{eff}<6$ eV show that the energy around q_y=0.21 becomes lower than that around q_y=0.90 and both states have lower energies than the collinear AFM-I state (q_y=1.00). In terms of the parameters obtained for $U_{eff}>6$ eV, however, the collinear AFM-I state becomes the ground state.

Now we evaluate $E(0,q_y,0)$ vs $(0,q_y,0)$ relations on the basis of noncollinear GGA+U electronic structure calculations using the WIENncm code.[21] In this method, the incommensurate spiral magnetic order is simulated without resorting to the supercell technique by using the generalized Bloch theorem.[25] The $E(0,q_y,0)$ vs $(0,q_y,0)$ relation calculated for the representative U_{eff} (i.e., 6 eV), presented in Fig. 4 as a dotted line, is quite similar to that found from the classical spin analysis. An important difference is that the noncollinear GGA+U calculations predict the spin-spiral state at q_y=0.20 to be slightly more stable that at q_y=0.95. The spin arrangement of the spin-spiral state at q_y=0.20 is illustrated in Figs. 1(b) and 1(c). In this state of zero total spin moment, the noncollinearity of the spin arrangement occurs not only between Cu spins but also between the O and Cu spins. Our calculations show substantial moments on the O sites, as found in previous studies.[11,13,26] From our calculation with U_{eff}=6.0 eV, the oxygen spin moment is $0.11\mu_B$, which agrees with the LDA+U result[27] and the experimental value (between $0.10\mu_B$ and $0.12\mu_B$).[13] Our noncollinear GGA+U electronic structure calculations with $U_{eff}>6$ eV or with $U_{eff}<6$ eV still show that the ground state is a spin-spiral state. Thus, with any reasonable U value, we predict a spin-spiral ground state for Li_2CuO_2.

From our noncollinear GGA+U calculations, the energy difference between the spin-spiral state at $\mathbf{q}=(0,0.20,0)$ and AFM-I state at $\mathbf{q}=(0,1.00,0)$ is very small (Fig. 4). In the case of U_{eff}=6 eV, the difference is 1 meV/Cu and deceases with increasing U_{eff}. From the classical spin analysis shown in Fig. 4, this energy difference is even smaller. As already pointed out, the $E(0,q_y,0)$ vs $(0,q_y,0)$ curve is sharp around q_y=0.20 but nearly flat around q_y=0.90–1.00. As a consequence, the states in the region of q_y=0.90–1.00 are nearly degenerate and are only slightly less stable than the spin-spiral ground state at $q_y\sim0.20$; namely, the density of states is much higher in the region of the AFM-I state than around the spin-spiral ground state. The latter provides a natural explanation for why the CuO_2 ribbon chains of Li_2CuO_2 do not exhibit a spiral-magnetic order despite that theCuO_2 chains are very similar in structure to those found in $LiCu_2O_2$ and $LiCuVO_4$, and Li_2CuO_2 has a spin-spiral ground state. In short, the AFM-I structure (q_y=1.00) is a collinear order arising from the occupation of many nearly degenerate states around q_y=0.90–1.10 and hence is an example of order by disorder.[14,15] The phase transition below 2.4 K, believed to be a transition to a spin-canted state, might arise from an increased population of the spin-spiral state at $\mathbf{q}=(0,0.20,0)$. What distinguishes Li_2CuO_2 from $LiCu_2O_2$ and $LiCuVO_4$ is the NNN interchain interaction J_4, which lowers the energy of the states around the AFM-I state and makes them nearly degenerate.

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