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Magnetic interactions in LiCu_2O_2 : Single-chain versus double-chain models

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The possible origin of the spiral spin structure in multiferroic LiCu_2O_2 is studied by calculating all relevant isotropic and anisotropic magnetic interactions in the material. The coupling constants are extracted from accurate *ab initio* quantum chemical calculations with an effective Hamiltonian theory. First, the anisotropic or Dzyaloshinskii-Moriya interactions are found to be negligible. Secondly, we obtain small isotropic interactions of the spin moments located on different chains, which classifies the material as a quasi-one-dimensional magnetic system. The intrachain isotropic interactions between nearest neighbors are relatively large and ferromagnetic, while second-neighbor interactions along the chain have antiferromagnetic character and are about half the magnitude of the former. This frustration leads to a spiral spin structure, which can be subjected to electric polarization.

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An important class of multiferroics is formed by the materials that simultaneously exhibit (anti)ferromagnetism and ferroelectricity. Particularly interesting are those materials in which these properties are coupled, since this can lead to mechanisms to control ferroelectricity by external magnetic fields or vice versa, as demonstrated by Kimura *et al.* in TbMnO_3 .¹ More recently, the LiCu_2O_2 ionic material has been studied by many scientists. Initially, attention was focused on its magnetic properties,^{2–4} but later the compound gained even more interest when ferroelectric behavior was evidenced.⁵ However, both the relative magnitude of the different magnetic interactions^{2–4,6,7} and the origin of the ferroelectric properties^{5,8–12} remain controversial. In particular, to what extent this material can be considered a single-chain one-dimensional system is still a subject of discussion.⁹ Based on a combination of a local density approach with modified intratomic Coulomb interactions (LDA + U) calculations and nuclear magnetic resonance (NMR) measurements, Gippius and co-workers² concluded that the interchain interactions are significantly smaller than the intrachain ones, while Masuda *et al.* reported large interchain interactions based on inelastic neutron scattering data.^{4,7} The latter picture gives rise to a double-chain frustrated model, where the frustration is due to interchain and next-nearest-neighbor intrachain antiferromagnetic interactions that compete with the ferromagnetic nearest-neighbor intrachain ones.

Different explanations for the origin of the spin current^{13,14} leading to ferroelectricity in this spiral magnet can be envisaged, involving (i) the inverse Dzyaloshinskii-Moriya (DM) mechanism; (ii) the frustration in either the single or double chains, which leads to spiral-magnetic ferroelectrics;⁵ or even (iii) the nonstoichiometry of the compound.⁸ Here, we check the relevance of the mechanisms (i) and (ii) by addressing the magnitude of the magnetic interactions in the stoichiometric structure. Furthermore, we bring additional information on the orientation of the local classical spin and on the spiral ordering by determining the orientation of the DM pseudovectors. One should note that different orientations for the spiral ordering have been proposed in the literature^{3,5,15} and that no consensus

has been reached yet on this question. The theoretical determination of the magnetic interactions in a nonstoichiometric structure would be highly interesting to address the role of (iii) in the multiferroicity of this material. However, unfortunately this task is not easily doable in practice due to the lack of information on the (nonstoichiometric) structure, and therefore it is beyond the scope of the present work.

To provide detailed, unbiased information on the magnetic interactions in the stoichiometric LiCu_2O_2 structure, *ab initio* wave-function-based calculations are used within the embedded cluster approach. Due to the local character of the magnetic couplings, accurate J_{ij} values can be obtained from embedded cluster calculations¹⁶ provided that the clusters and embedding are consistently chosen, and that accurate N -electron wave functions are used. To address the relevance of the clusters and their embedding schemes, it is useful to compare the results obtained with the embedded clusters with periodic calculations at a given level of theory. This comparison is usually done at the unrestricted Hartree-Fock (UHF) level with an Ising Hamiltonian ($\hat{H}_{\text{Ising}} = \sum_{ij} J_{ij}^{\text{Ising}} \hat{S}_i^z \hat{S}_j^z$). However, an accurate determination of the magnetic couplings requires a rigorous incorporation of the electron correlation in the theoretical treatment, as analyzed in detail by Calzado *et al.*^{17–19} This requires a variational treatment of all the excited Slater determinants that contribute to the energy difference between the magnetic states at second order of perturbation, i.e., one has to invoke at least difference-dedicated configuration interaction (DDCI).²⁰ Once accurate energy differences between the magnetic states are obtained, the magnetic coupling parameters are extracted with the effective Hamiltonian theory²¹ by mapping the energies and projected wave functions onto the Heisenberg-Dirac-van Vleck (HDVV) Hamiltonian ($\hat{H} = \sum_{ij} J_{ij} \hat{S}_i \cdot \hat{S}_j$). The DM pseudovector can be computed in a similar way when the spin-orbit coupling is accounted for in the calculation.^{22,23}

The experimental structure of the rhombohedral LiCu_2O_2 crystal²⁴ as shown in Fig. 1 is used in all the calculations. LiCu_2O_2 is a mixed-valence compound: double LiCu_2O_2 layers containing (formally) Cu(II) ions are separated by layers of nonmagnetic Cu(I) ions. The intrachain interactions occur

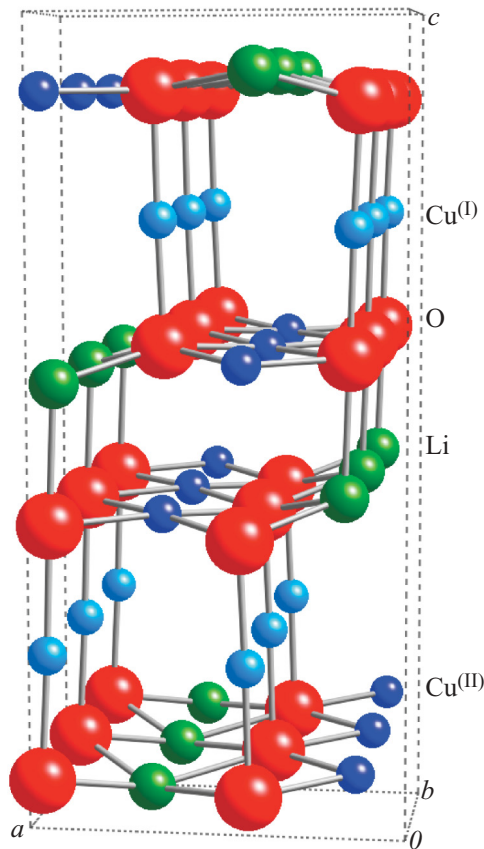


FIG. 1. (Color online) Crystal structure of LiCu_2O_2 .²⁴

along the b axis, as can be seen in Fig. 1. Intrachain and interchain clusters containing two and three copper centers have been considered to extract the magnetic interactions. Clusters 1 and 1b are intrachain clusters with two or three copper centers, respectively. They are depicted in Fig. 2. In cluster 1b, the three copper ions are effectively coupled through the nearest-neighbor interaction J_1 and the next-nearest-neighbor interaction J_2 (see Fig. 3). Clusters 2 and 2b are interchain clusters containing either two or three copper centers and are represented in Fig. 4. In this last cluster, the three copper ions occupy the corners of an isosceles triangle, interacting through J_1 along the chain and twice through J_{DC} among different chains, where DC stands for the “double-

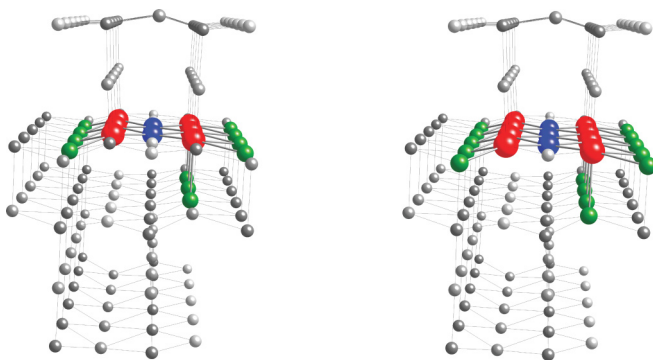


FIG. 2. (Color online) Cluster 1 (left) and cluster 1b (right). Explicitly treated atoms in blue (copper), red (oxygen), and green (lithium); other atoms in gray.

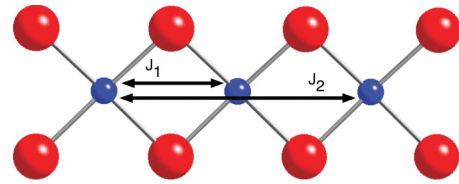


FIG. 3. (Color online) Magnetic interaction paths for J_1 and J_2 in cluster 1b. Explicitly treated copper atoms in blue and oxygen atoms in red; lithium ions are not shown for clarity.

chain” interaction (see Fig. 5). In addition to the copper ions, the clusters contain all oxygen ions directly coordinated to the metal ions, as well as the first shell of lithium ions. The necessity of treating explicitly this shell of lithium ions was previously evidenced in the closely related Li_2CuO_2 system, for which it was shown that the quality of the treatment of the lithium ions affects the spin density on the bridging oxygen atoms, and hence strongly affects the next-nearest neighbor magnetic interactions while moderately affecting the nearest-neighbor ones.^{25,26} The next shell of oxygen and copper ions is represented by *ab initio* model potentials (AIMPs) that have been optimized through the self-consistent field embedded ion (SCEI) procedure.²⁷ A large set of point charges located at lattice sites around the cluster has been optimized to accurately fit the Madelung potential on a grid centered in the cluster. This way of defining the clusters and their embeddings has been used successfully in many other works dealing with effective magnetic interactions, while only recently has it become possible to include anisotropic effective interactions.²³

It is good practice in embedded cluster studies to validate the employed clusters and embeddings. In the present study, this is done by comparing the outcomes of UHF and unrestricted density functional theory with the hybrid B3LYP functional, UDFT(B3LYP), obtained from periodic and cluster approaches. The periodic calculations are performed with the CRYSTAL09 program package.²⁸ The cluster calculations are performed with the MOLCAS code.²⁹ The same contracted Gaussian-type basis sets have been used for both types of calculations, i.e., $\text{Cu}(6s5p2d)$, $\text{O}(3s2p)$, and $\text{Li}(2s1p)$.³⁰ As expected, the periodic calculations confirm the mixed-valence character of the compound. We then considered different supercells and the above-described clusters to extract nearest

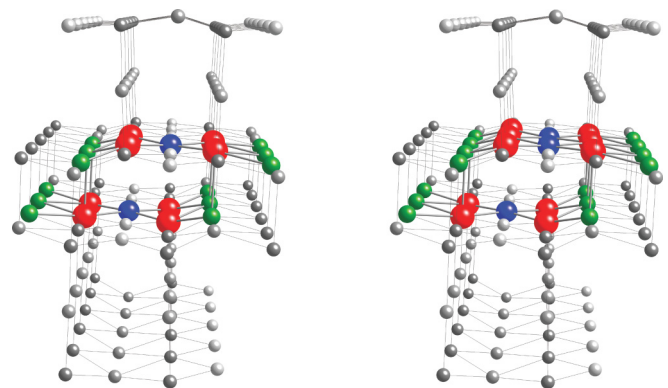


FIG. 4. (Color online) Cluster 2 (left) and cluster 2b (right). Explicitly treated atoms in blue (copper), red (oxygen), and green (lithium); other atoms in gray.

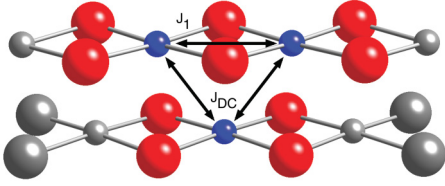


FIG. 5. (Color online) Magnetic interaction paths for J_1 and J_{DC} in cluster 2b. Explicitly treated copper atoms in blue and oxygen atoms in red; lithium ions are not shown for clarity; other atoms in gray.

intrachain (J_1^{Ising}) and interchain ($J_{\text{DC}}^{\text{Ising}}$) interactions (following the notations of Seki *et al.*⁹) of the Ising model. The results are presented in Table I. The magnetic coupling parameters extracted from the embedded cluster calculations closely reproduce the trends observed in the periodic calculations at both levels of theory. A large ferromagnetic intrachain nearest-neighbor interaction (i.e., a large negative J_1 value) is combined with a smaller antiferromagnetic interchain interaction (i.e., a small positive J_{DC} value). As expected, the B3LYP coupling parameters are much larger than the ones obtained at the UHF level.³¹ The UHF and B3LYP results are known to give very different coupling parameters, and none of these levels of theory is expected to give sufficiently accurate descriptions of the magnetic couplings. Here, we present both UHF and B3LYP results to show that the reasonably good agreement of the cluster calculations with the periodic ones is independent of the levels of theory used in the calculation, although the computed magnetic couplings are strongly dependent on these. The use of other functionals than the B3LYP considered here could lead to important changes in the calculated magnitude of the couplings.³² However, this does not affect the agreement found between periodic and embedded cluster calculations, since both approaches would suffer very similar variations upon changing the functional. It is then concluded at this stage that the clusters and embeddings are consistently built, and that embedded cluster calculations provide a good description of the magnetic interactions calculated at the same level of approximation in the LiCu_2O_2 crystal. Of course UHF and UDFT(B3LYP) results cannot be used to obtain quantitative estimates of the ratios between different (competing) interactions.²³

To provide quantitative estimates of the magnetic coupling parameters, we give an accurate description of the N -electron wave functions in the clusters by applying the DDCI scheme.²⁰ This scheme, which is implemented in the CASDI code,³³ provides an efficient way to include electron correlation in the *ab initio* description of the electronic structure. It is similar to the method recently described by Hozoi and co-workers^{34,35}

TABLE I. UHF and UDFT(B3LYP) magnetic coupling constants (in meV) obtained from cluster and periodic calculations. The Ising model Hamiltonian $\hat{H}_{\text{Ising}} = \sum_{ij} J_{ij}^{\text{Ising}} \hat{S}_i^z \hat{S}_j^z$ is used to extract J values from the energy eigenvalues.

| UHF/UDFT(B3LYP) | Cluster | Periodic |
|--------------------------------|--------------|--------------|
| J_1^{Ising} | -16.0/ -42.2 | -10.4/ -33.6 |
| $J_{\text{DC}}^{\text{Ising}}$ | 0.3/0.3 | 0.8/0.8 |

TABLE II. CASSCF magnetic coupling constants (in meV) obtained from embedded clusters with two and three Cu ions. The HDVV model Hamiltonian $\hat{H}_{\text{HDVV}} = \sum_{ij} J_{ij} \hat{S}_i \cdot \hat{S}_j$ is used to extract J values from the energy eigenvalues.

| | J_1 | J_2 | J_{DC} |
|------------|-------|-------|-----------------|
| Cluster 1 | -4.8 | | |
| Cluster 1b | -4.8 | 1.1 | |
| Cluster 2 | | | -0.1 |
| Cluster 2b | -4.8 | | 0.0 |

to study the d - d transitions in related cuprate compounds. The applied basis set to describe the one-electron functions is especially designed to recover the semicore and valence electron correlation. We use atomic natural orbitals relativistic with core correlation (ANO-RCC) basis sets³⁶ with the following contractions: Cu(6s5p4d), O(4s3p1d), and Li(2s). The complete active space self consistent field (CASSCF) and DDCI results are reported in Tables II and III, respectively. As expected, CASSCF only accounts for about 30% of the DDCI J_1 value, due to the lack of dynamic correlation. J_2 is even more drastically affected by the introduction of dynamic correlation (from 1.1 meV at the CASSCF level to 7.1 meV at the DDCI level), while J_{DC} is very small at both CASSCF and DDCI levels. Experience has shown that CASSCF usually accounts for 20–30 % of the J values, while the more accurate DDCI results usually account for 70–90 % of these values. Therefore, we will use the DDCI results in the rest of the discussion.

The cluster wave functions are spin eigenfunctions, and we map the energies on the Heisenberg Hamiltonian. In all the clusters where J_1 is accessible, a similar value of about -15 meV is obtained, confirming the large ferromagnetic intrachain nearest-neighbor interaction. The intrachain next-nearest-neighbor interaction, J_2 , is found to be antiferromagnetic and of sufficient magnitude to compete with the ferromagnetic J_1 , and its value is in agreement with experimental and previous theoretical estimates. Our results for the different magnetic couplings are indeed in good agreement with the LDA + U calculations of Gippius *et al.* ($J_1 = -13.9$ meV, $J_2 = 10.1$ meV, and $J_{\text{DC}} = 0.5$ meV).²⁴ The obtained ratio of J_2 and J_1 is expected to lead to a long-range spiral-type ordering of the spins in a classical picture.³⁷

Due to the symmetry of the crystal,²⁴ no interchain DM interaction is expected, while it may be present for neighboring ions located on the same chain.^{38,39} Following the strategy applied earlier in the CuO material,²³ we computed the DM pseudovector in cluster 1. In this cluster, a symmetry plane

TABLE III. DDCI magnetic coupling constants (in meV) obtained from embedded clusters with two and three Cu ions. The HDVV model Hamiltonian $\hat{H}_{\text{HDVV}} = \sum_{ij} J_{ij} \hat{S}_i \cdot \hat{S}_j$ is used to extract J values from the energy eigenvalues.

| | J_1 | J_2 | J_{DC} |
|------------|-------|-------|-----------------|
| Cluster 1 | -17.6 | | |
| Cluster 1b | -14.8 | 7.1 | |
| Cluster 2 | | | 0.1 |
| Cluster 2b | -14.1 | | -0.1 |

is present in the ac direction, and this symmetry plane can transform one magnetic center into another one. As a consequence, the DM vector is expected to be along this ac plane. The determination of the orientation of the DM vector can give important information on the orientation of the local classical spins and hence on the spiral ordering: if the DM vector is found in the a direction, then the spins should be oriented within the bc plane; if the DM vector is found in the c orientation, the spins should be oriented within the ab plane; and if the DM vector has nonzero components in both a and c orientations, then the spins are oriented in a tilted plane in between the ab and bc planes. However, our *ab initio* calculations show that the DM vector is extremely small ($|\vec{d}| < 0.02$ meV) and falls below the intrinsic numerical accuracy of the method. In fact, the structure is rather close to having inversion symmetry located between two adjacent Cu ions along the chains. Therefore, it is not unexpected that the DM vector almost vanishes and that the orientation of the DM vector cannot be used to give further information on the spiral ordering in this compound. At this stage, one could argue that the orientation of the local classical spins in this compound is still an open question, but one could also question the role played by the DM interaction on the properties of the compound given the smallness of the calculated DM vector.

Another important result concerns the magnitude of the interchain interactions, i.e., the magnitude of J_{DC} . As can be seen

in Table III, in none of our calculations was a sufficiently large J_{DC} value obtained to induce competition with the intrachain interactions. According to our long-standing experience, this result is not sensitive to the extension of the clusters. The two orders of magnitude difference indicates that the compound is essentially a frustrated single-chain one-dimensional system, as suggested by Gippius *et al.*² The hypothesis of a frustrated double-chain system, as suggested by Masuda *et al.*,^{3,4} is not supported by our calculations. Since the interchain interactions are negligible in this system, one would consider that the intrachain couplings are responsible for the multiferroicity. However, despite the frustration observed in this chain, the DM interaction is almost negligible. As a consequence, the DM interaction is not likely to cause any significant electric polarization and cannot be the main origin of the multiferroicity in LiCu_2O_2 . The multiferroic behavior of LiCu_2O_2 can then come from the frustration along the b orientation and/or be linked to the nonstoichiometry of the crystal samples,^{3,8,11} but not from direct DM interaction.

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