

## Calculated magnetocrystalline anisotropy and magnetic moment distribution in $\text{Li}_2\text{CuO}_2$

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We calculate the magnetic properties of the edge-sharing cuprate compound  $\text{Li}_2\text{CuO}_2$  having an antiferromagnetic arrangement of ferromagnetic  $\text{CuO}_2$  chains in the framework of density functional theory. The magnetocrystalline anisotropy energy is obtained by means of a relativistic band-structure calculation within the local spin density approximation (LSDA). In agreement with experiment, the magnetic moments point into the crystallographic  $\vec{a}$  direction perpendicular to the  $\text{CuO}_4$  plaquettes, but the calculated magnetic anisotropy energy  $E(\vec{m}\parallel\vec{c})-E(\vec{m}\parallel\vec{a})=0.34$  meV overestimates the experimental value. The influence of strong electron correlation on the magnetic moments is calculated by the LSDA+ $U$  method reducing the oxygen moment to  $0.1 \mu_B$ .

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The discovery of high-temperature superconductivity led to a broad interest in cuprate compounds. Many one- and two-dimensional cuprate compounds were synthesized and studied, especially as playgrounds to investigate low-dimensional magnetism. The magnetic behavior of cuprates is usually very rich<sup>1</sup> and cannot be understood in terms of isotropic Heisenberg models alone. So, one finds in certain cases a pronounced magnetocrystalline anisotropy, or a distribution of the magnetization density over both the copper and the oxygen sites.<sup>2,3</sup> Cuprate compounds can be divided into a class containing  $180^\circ$  Cu-O-Cu bonds as in corner-sharing chains or in the standard  $\text{CuO}_2$  plane, and into another one with Cu-O-Cu bonds close to  $90^\circ$  as in edge-sharing cuprates. A representative example for the latter class is  $\text{Li}_2\text{CuO}_2$  with a number of unusual aspects in its magnetic behavior.

The magnetic structure of  $\text{Li}_2\text{CuO}_2$  has been determined by neutron diffraction<sup>4</sup> and consists of ferromagnetic chains running along the crystallographic  $\vec{b}$  direction that are arranged antiferromagnetically. Measuring the spin-wave dispersion by inelastic neutron scattering<sup>5</sup> a large gap at the zone center had been found pointing to a pronounced magnetocrystalline anisotropy which was also seen in antiferromagnetic resonance (AFMR).<sup>6</sup> Theoretically, an antiferromagnetic arrangement of ferromagnetic chains was found in the LSDA calculation of Ref. 2 where additionally a considerable magnetic moment at the oxygen sites of  $0.2 \mu_B$  was predicted. This and other LSDA studies<sup>7,8</sup> point also to considerable interchain couplings and frustration effects which were confirmed in a quantum chemical approach.<sup>9</sup> The oxygen moment formation was experimentally confirmed by muon spin rotation<sup>10</sup> and by a very detailed neutron diffraction experiment.<sup>3</sup> The latter data showed also that the LSDA prediction overestimates the oxygen moment by a factor of 2. A first LSDA+ $U$  study,<sup>11</sup> taking into account the strong Coulomb repulsion at the copper site, seemed *not* to improve the LSDA result, reducing the oxygen moment from  $0.22 \mu_B$  to only  $0.21 \mu_B$ . However, we will show here that a proper application of the LSDA+ $U$  method leads indeed to im-

proved oxygen moments, being then in agreement with experiment. Another purpose of our work is the density functional study of magnetocrystalline anisotropy in  $\text{Li}_2\text{CuO}_2$ .

Magnetocrystalline anisotropy is a purely relativistic effect and requires the inclusion of spin-orbit (SO) coupling in the Hamiltonian. For cuprates, until now, only perturbation theory with respect to the SO coupling and with respect to the kinetic energy in a multiband Hubbard-type Hamiltonian was used to provide the form and the parameters of the anisotropic spin Hamiltonian.<sup>1</sup> In such a kind of approach the magnetocrystalline anisotropy of the rectangular Cu-O-Cu bond was found to be surprisingly large<sup>12,13</sup> compared to other cuprates. The theoretical analysis of the magnetocrystalline anisotropy within the perturbative approach, however, is hindered by a large number of hopping and interaction parameters that have to be obtained by other means. Therefore, an alternative approach would be highly desirable. Here, we will show that reasonable values of the magnetocrystalline anisotropy energy (MAE) of  $\text{Li}_2\text{CuO}_2$  can be obtained by relativistic density functional calculation in a straightforward way. To our knowledge, no other *ab initio* like calculation of MAE has ever been reported for any cuprate material.

The *ab initio* calculation of the magnetocrystalline anisotropy energy (MAE) has meanwhile a long history in the field of itinerant magnetism. Due to the relative smallness of the MAE's—usually being in the range from a few  $\mu\text{eV}$  to a few meV per atom and several orders of magnitude smaller than the total energies involved—their evaluation puts strong requirements on the accuracy of the numerical scheme involved. Early calculations of the MAE of transition metal compounds based on the magnetic force theorem have been performed by Daalderoop *et al.*<sup>14,15</sup> and later on by several other authors.<sup>16–18</sup> More recently, also total energy calculations of the MAE with more accurate full potential band structure schemes have become accessible.<sup>19,20</sup> These calculations usually result in a semiquantitative agreement with experiment, i.e., the correct order of magnitude and the correct easy axis is predicted. For certain compounds the inclusion of orbital polarization corrections<sup>21</sup> to LSDA lead to a

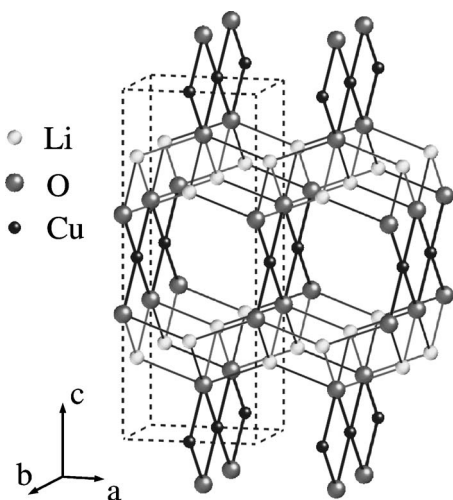


FIG. 1. The crystal structure of  $\text{Li}_2\text{CuO}_2$ . The edge sharing chains are running in the  $\vec{b}$  direction. The easy axis is along  $\vec{a}$ . The orthorhombic primitive cell is shown in dashed lines.

considerable quantitative improvement of the agreement between the calculated and experimental values. These corrections, however, are not relevant for the present calculations, where only one hole is present in the Cu  $3d$  shell. For a more complete overview on this topic, see for example Ref. 22.

The calculations were mainly performed within the full-potential local-orbital (FPLO) band structure scheme,<sup>23</sup> taking into account SO coupling by its relativistic version (RFPLO) (Refs. 24 and 25) or correlation effects by the FPLO implementation<sup>26</sup> of the LSDA+ $U$  method.<sup>27</sup> In the FPLO method a minimum basis approach with optimized local orbitals is employed, which allows for accurate and efficient total energy calculations. For the present calculations we

used the following basis set: Li  $1s:2s2p;3d$ , Cu  $3s3p:4s4p3d$ , and O  $2s2p;3d$  states. The inclusion of the Li  $1s$  and Cu  $3s,3p$  semicore states into the valence was necessary to account for non-negligible core-core overlap, Li  $3d$  and O  $3d$  states were used to improve the completeness of the basis set. The site-centered potentials and densities were expanded in spherical harmonic contributions up to  $l_{\max}=12$ . The LSDA parametrization of Perdew and Zunger<sup>28</sup> was used. For the calculation of the MAE of  $\text{Li}_2\text{CuO}_2$  we used the relativistic version of the FPLO code (RFPLO-1.6.2). In the RFPLO method, the four-component Kohn-Sham-Dirac equation for the crystal, which includes spin-orbit coupling up to all orders, is solved in a collinear approximation. The scheme was recently applied to a number of actinide compounds<sup>25,29</sup> and to the calculation of the MAE of transition metal compounds<sup>25,30</sup> in good agreement with experiment and other state-of-the-art calculations. The calculation of the MAE usually requires a large number of  $\vec{k}$  points for the BZ integration, especially for metals. We checked the convergence of the total energies with respect to numerical parameters and  $\vec{k}$ -space integrations with a series of calculations with up to about 15000  $\vec{k}$  points in the full Brillouin zone (BZ). Nevertheless, we found that the MAE was converged quite rapidly because of the insulating ground state (with numerical fluctuations of less than  $3 \times 10^{-11}$  eV for more than 900  $\vec{k}$  points). Another check of the accuracy of our calculated magnetocrystalline anisotropy energies was the comparison of the RFPLO data with those obtained within the WIEN2k code, i.e., using the linearized augmented plane wave (LAPW) method and spin-orbit coupling.<sup>32</sup> As will be presented below, both band-structure schemes (using completely different basis functions) lead to very similar values.

The edge-sharing cuprate compound  $\text{Li}_2\text{CuO}_2$  crystallizes

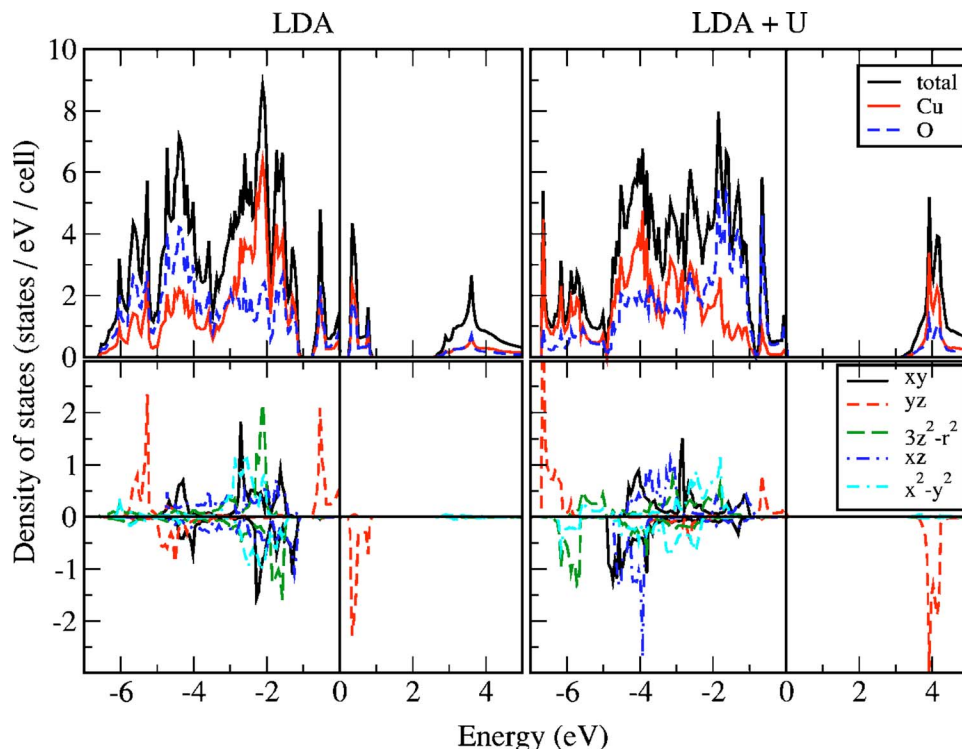


FIG. 2. (Color online) Total and partial DOS (top) as well as Cu  $3d$  orbital resolved DOS (bottom) of  $\text{Li}_2\text{CuO}_2$  calculated within the LSDA (left) and LSDA+ $U$  schemes (right).

in a body-centered orthorhombic symmetry ( $Immm$ ) with lattice constants  $a=3.6615$  Å,  $b=2.8628$  Å,  $c=9.3926$  Å, and  $\text{CuO}_2$  chains running along the  $\vec{b}$  direction.<sup>4</sup> In the antiferromagnetic case the centering is lost, and the Bravais lattice becomes a simple orthorhombic lattice with symmetry  $Pmmm$  (see Fig. 1). Our LSDA calculations correctly reproduce the antiferromagnetic insulating ground state, but with a too small value for the band gap (Fig. 2). The ferromagnetic solution in FPLO has a total spin moment of  $0.93 \mu_B$ , with copper and oxygen contributions of  $0.55$  and  $0.19 \mu_B$ , respectively, similar to previously reported LSDA calculations.<sup>2</sup> The antiferromagnetic ordering of ferromagnetic  $\text{CuO}_2$  chains reduces the total energy by about 9 meV compared to a ferromagnetic arrangement of the chains. The corresponding magnetic moments, calculated with RFPLO for different magnetization axes are presented in Table I. The orbital moment on the Cu sites shows a pronounced anisotropy, while the other moments are nearly independent of the magnetization axis.

We also calculated the total energies for the antiferromagnetic ground state with the magnetic moment aligned along the three different crystallographic axes. The energy difference  $\Delta E = E[001] - E[100] = 0.334$  meV/f.u. determines the MAE, while the energy difference  $E[010] - E[001] \approx 0.005$  meV/f.u. is found to be negligible. The so determined easy  $\vec{a}$  axis coincides with the easy axis found by antiferromagnetic resonance.<sup>6</sup> The LAPW+SO calculation gives  $\Delta E = 0.338$  meV in very good agreement with RFPLO. In that calculation we used  $2000 \vec{k}$  points and a cutoff parameter  $\text{RKmax}=8$ . The agreement between both methods shows that our LSDA values of the MAE are converged with respect to all numerical details.

The LSDA oxygen moment of  $0.19 \mu_B$  considerably exceeds the experimental value of  $0.10 \mu_B$ . That can be understood since LSDA usually overestimates hybridization effects in cuprates. To improve the result, we performed a LSDA+ $U$  calculation with the Slater Coulomb parameters  $F_0=8$  eV,  $F_2=8.6$  eV, and  $F_4=5.4$  eV at the copper sites, close to literature values<sup>26</sup> and under the constraint that  $J = (F_2 + F_4)/14 = 1$  eV and  $F_2/F_4 = 1.6$  as for atoms. We used the ‘‘around mean field’’ version of LSDA+ $U$  with orthogonal projection and  $7200 \vec{k}$  points in the full BZ. The lattice

TABLE I. Calculated spin ( $m^s$ ) and orbital ( $m^l$ ) moments of  $\text{Li}_2\text{CuO}_2$ , using the RFPLO method within the LSDA scheme.

	$m_{\text{Cu}}^s$	$m_{\text{O}}^s$	$m_{\text{Cu}}^l$	$m_{\text{O}}^l$
[010]	0.510	0.193	0.028	0.002
[001]	0.510	0.193	0.027	0.002
[100]	0.511	0.193	0.106	0.006

parameters were not changed and a magnetic structure of antiferromagnetically arranged ferromagnetic chains was calculated. In such a way we obtained the following magnetic moments:  $m_{\text{Cu}}=0.75 \mu_B$ ,  $m_{\text{O}}=0.11 \mu_B$ , and  $m_{\text{Li}}=0.002 \mu_B$ . The oxygen magnetic moment is in good agreement with the experimental data,<sup>3</sup> but also with the quantum chemical calculation of Ref. 9. The discrepancy with the previous LSDA+ $U$  calculation by Tanaka *et al.*<sup>11</sup> can be explained by the different  $U$  values. A value of  $U=4$  eV as used in Ref. 11 is too small to obtain a realistic electronic structure in cuprates. The density of states (DOS) presented in Fig. 2 shows clearly that the gap value increases from 0.25 eV (in LSDA) to the more realistic value of 3.2 eV in LSDA+ $U$ . The LSDA-DOS agrees well with the previous calculation of Weht and Pickett.<sup>2</sup> The orbital resolved DOS shows that the relevant band at the Fermi level is built up of the copper  $3d_{yz}$  orbital hybridized with oxygen  $2p$ . But, interestingly, the orbital character changes: in LSDA the oxygen content is nearly identical in the occupied valence and the empty conduction band, whereas in LSDA+ $U$  the valence band has predominantly oxygen character in difference to the copper character of the conduction band as expected in a charge-transfer insulator.

To provide more insight into measurable quantities we present in Fig. 3 a comparison of the spin densities of both approaches. The symmetry of the  $3d_{yz}$  orbital and the distribution of the spin density onto copper and oxygen sites is nicely visible in both cases. The Coulomb correlation in LSDA+ $U$  leads to a redistribution of spin density from the oxygen to the copper sites and the so obtained spin density agrees well with the neutron diffraction measurement of Ref. 3. Please note that the theoretical spin density is slightly negative at the copper site due to the Cu  $4s$  contribution.

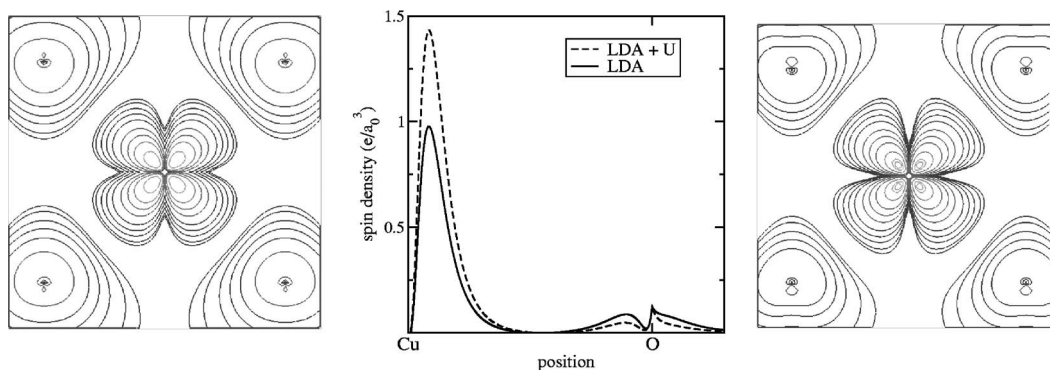


FIG. 3. Spin density in the plane of one  $\text{CuO}_4$  plaquette (copper at the center) calculated within the LSDA (left) and the LSDA+ $U$  method (right). The spin density of both approaches along the line Cu-O is compared in the middle panel. A logarithmic mesh between 0.001 ( $e/a_0^3$ ) and the corresponding maximum value is used in the contour plots.

TABLE II. Calculated and measured values of the magnetocrystalline anisotropy energy (MAE)  $\Delta E = E[001] - E[100]$  in  $\text{Li}_2\text{CuO}_2$ .

Method	Reference	$\Delta E/\text{meV}$
Theory		
RFPL0	Present work	0.334
LAPW+SO	Present work	0.338
Perturbation theory	Ref. 13	0.32
Experiment		
AFMR	Ref. 6	0.078
Neutron scattering	Ref. 5	0.078
Magnetization jump	Ref. 31	0.045

Let us compare the present result for the MAE with perturbation theory and with measurements (see Table II). The perturbation theory for the standard  $90^\circ$  Cu-O-Cu bond<sup>13</sup> resulted in the symmetric anisotropy part of the Hamiltonian for one bond between spin A and spin B at neighboring copper sites of the form:

$$H_{AB}^{\text{aniso}} = J_{\parallel} \hat{S}_A^{\parallel} \hat{S}_B^{\parallel} + J_{\perp} \hat{S}_A^{\perp} \hat{S}_B^{\perp} + J_z \hat{S}_A^z \hat{S}_B^z \quad (1)$$

with the  $\vec{z}$  axis perpendicular to the  $\text{CuO}_4$  plaquettes, i.e., identical to the crystallographic  $\vec{a}$  direction. Neglecting the small difference between  $J_{\parallel}$  and  $J_{\perp}$ , the following parameters were found:  $J_{\parallel} = J_{\perp} = 0.65$  meV and  $J_z = -0.65$  meV. Taking for simplicity the classical value of the spin  $S = |\vec{S}| = 1/2$  for the average of the quantum value  $\vec{S} = \langle \hat{S} \rangle$  we find from (1) for the energy difference  $\Delta E = E(\vec{S} \perp z) - E(\vec{S} \parallel z) = (J_{\parallel} - J_z)/4 = 0.32$  meV.

Experimental information about the MAE was found from AFMR.<sup>6</sup> Neglecting the small difference between  $H_{A1}$  and  $H_{A2}$ , an anisotropy field  $H_A$  of roughly 3 T was measured. Taking into account the averaged magnetization  $m = |\vec{m}| = 0.9 \mu_B (\vec{m} = g \mu_B \langle \hat{S} \rangle)$  such an anisotropy field corresponds to a MAE (per Cu site) of  $\Delta E = (m \cdot H_A)/2 = 0.078$  meV. Analogously, the neutron scattering experiment<sup>5</sup> determined an anisotropy parameter  $D = -0.31$  meV, which means for the MAE  $\Delta E = -DS^2 = -D/4 = 0.078$  meV, in agreement with the AFMR data. A third, independent experimental information about the MAE in  $\text{Li}_2\text{CuO}_2$  was recently obtained by magnetization measurements in the magnetic field.<sup>31</sup> At the temperature of 2.5 K a MAE of 0.045 meV was measured from the magnetization jump at the spin-flop field. At 2.5 K this value shows some temperature dependence and will probably slightly increase towards zero temperature.

The available theoretical results overestimate the measured anisotropy energy by a factor of 4, roughly, and they give only a qualitative but not a quantitative description of

the magnetocrystalline anisotropy in  $\text{Li}_2\text{CuO}_2$ . The reasons for the discrepancies are different, however. Within the perturbation theory,<sup>1,12,13</sup> the Hubbard correlation is properly treated. The lack of quantitative agreement is not so surprising taking into account the restricted and indirect knowledge of crystal-field, spin-orbit and hopping parameters, as well as the limitations of fourth order perturbation theory. On the other hand, in the LSDA calculations, it is probably the insufficient treatment of the Hubbard correlation which causes the deviation. One might speculate that larger gap values would decrease the MAE but this remains to be shown by a calculation taking into account relativistic and correlation effects on equal footing.

The present study concentrates on the anisotropy energies and oxygen moments for which a certain consensus about the experimental values has been obtained. It should be noted that there is a discussion about the numerical values of the exchange couplings in the ferromagnetic chain and between chains.<sup>2,5,9</sup> These exchange couplings can be derived from the LSDA and the LSDA+ $U$  energy differences of different magnetic configurations as well as from other methods. Both our LSDA and LSDA+ $U$  calculations lead to exchange couplings which are in agreement with antiferromagnetically coupled ferromagnetic chains with a ferromagnetic exchange between nearest neighbors of several meV. Such a nearest neighbor exchange is in rough agreement with the quantum-chemical calculation of Ref. 9 but much larger than the value derived from neutron scattering (Ref. 5). A detailed, thorough discussion of exchange couplings, however, demands a critical comparison of different methods, which is outside the scope of the present work and will be presented elsewhere (Ref. 33). Also, the magnetic anisotropy and the magnetization distribution within the chains are nonsensitive to the spin arrangements between them. Furthermore, the possibility of a noncollinear magnetic state as indicated by the experimental results in Refs. 3 and 10 was not explored in our calculation.

In summary, we have demonstrated that the magnetocrystalline anisotropy energy in strongly correlated and insulating cuprate compounds can be computed very directly within density functional theory in a semiquantitative manner. Already LSDA delivers reasonable values, provided we can start from the correct magnetic ground state. That is usually the case for edge sharing cuprates which was demonstrated here for  $\text{Li}_2\text{CuO}_2$ . We obtained the correct easy axis and a reasonable agreement for the MAE. We also calculated the influence of Coulomb correlations on the oxygen moments by the LSDA+ $U$  method leading to a considerable improvement of the LSDA values.

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