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Magnetic Ordering in CuO from First Principles: A Cuprate Antiferromagnet with Fully Three-Dimensional Exchange Interactions

Alessio Filippetti and Vincenzo Fiorentini

SLACS INFM-CNR and Dipartimento di Fisica, Università di Cagliari, I-09042 Monserrato (Ca), Italy
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We investigate the interplay of bonding and magnetism in CuO by a first-principles self-interaction-free density-functional approach. Our analysis reveals that, at variance with typical low-dimensional cuprates, a fully three-dimensional view of the exchange interactions is needed to describe accurately the magnetic ground state and low-energy excitations in CuO. The apparent one-dimensional behavior of antiferromagnetic order is due to the presence of a single spin-polarized hole of d_z^2 character. This induces a strongly anisotropic magnetic ordering built up by ferromagnetic (x, y) layers, and antiferromagnetic chains along z, with exchange interactions of similar magnitude.

Understanding the chemistry of copper-oxygen interactions is one of the outstanding open issues of solid-state physics, due to the obvious implications with the physics of high-T_c superconducting materials, whose basic units are Cu-O chains or layers. Although there is clear experimental evidence of a strongly antiferromagnetic Cu-Cu spin coupling in both the insulating parent compounds and, residually, in the doped superconducting phases [1], a consistent picture relating chemical bonding, energetics, and magnetic ordering in Cu-O systems is still missing.

Arguably, one reason for this is the scarcity of reliable and manageable first-principles approaches [2] to this problem. Indeed, the local spin-density approximation (LSDA) to density-functional theory describes most copper oxides (including CuO [3]) as diamagnetic metals. On the other hand, beyond-LSDA theories applied so far [4] to cuprate systems are either not practicable for large systems, or depend on empirical parameters whose values crucially affect quantitative predictions. In this Letter, we apply to the prototypical cuprate CuO the pseudo-*SIC* method [5] based on an approximate form of self-interaction-corrected Kohn-Sham pseudopotential Hamiltonian [6], already successfully applied to a variety of ionic and strongly-correlated materials. The pseudo-*SIC* method is free of *ad-hoc* parameters, but it preserves the moderate computational cost and the conceptual simplicity of LSDA, and it enables us to produce a satisfactory microscopic picture of magnetic ordering in CuO.

The conceptual foundation of magnetism in cuprates lies on the Anderson theory of superexchange and the derived Goodenough-Kanamori-Anderson rules (GKA) [7]. A popular computational attack based on these concepts is the spin-1/2 single-band Hubbard Hamiltonian [8] or variants thereof (such as three-band model [9] or t-J model [10]). However, its predictive power is limited to idealized—albeit important—cases such as unidimensional Cu-O chains or bi-dimensional CuO_2 plates [11,12]. For real materials, first-principles calculations are called for

to provide quantitative predictions of the full three-dimensional crystal structure and electronic properties. For example, in $GeCuO_3$, with nearly CuO_2 square planar coordination, we might expect a ferromagnetic (FM) Cu-Cu first-neighbor coupling [13] but in fact the interaction is antiferromagnetic (AF) due [14] to perturbation by side groups (i.e., Ge^{4+} ions); in Li_2CuO_2, correctly described as insulating antiferromagnet by LSDA [15], AF ordering can only be understood as an interplay of first- and second-neighbor intra- and interchain couplings.

CuO is even more peculiar: while most cuprates are built by an assembly of one- or two-dimensional Cu-O units, CuO is boldly three dimensional. The nominal configuration $Cu^{2+}O^{2-}$ leaves a single d electron unpaired, inducing both Cu magnetic moments and a cubic-to-monoclinic structural distortion [16,17]. Experiments show AF ordering below $T_N \sim 220$ K, resulting from FM layers compensating along the $[10\bar{1}]$ direction of the cubic unit cell [17]. The AF superstructure, schematized in Fig. 1, is then a
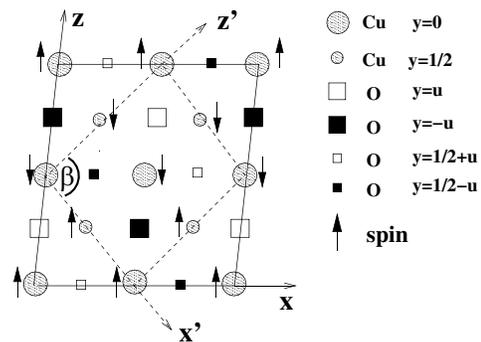
FIG. 1.   Side view of monoclinic CuO cell: (a, c) plane and b axis are parallel and orthogonal to the sheet, respectively. Arrows show the AF$_z$ ordering, made of FM layers compensating each other along z. Dashed axes x', z' show the diamagnetic cell (notice that $z = [10\bar{1}]$ in x', z' coordinates). The cell parameters are $a = 6.346$ Å, $b/a = 0.5387$, $c/a = 1.18$, beta $= 99.54°$. $u = 0.1684$ is an internal parameter [16].

$\sqrt{2} \times 1 \times \sqrt{2}$ replica of the cubic cell, and contains 8 formula units. Taking x and z parallel to the (a, c) vectors of the AF cell, the AF ordering occurs along z, a structure which we label AF_z. A three-dimensional view of the AF_z structure is shown in Fig. 2.

The Cu ions are arranged in a distorted fcc coordination, and the O-centered tetrahedra are distorted in such a way that each Cu lies on a plane formed by its four oxygen neighbors. The rather high Néel temperature indicates strong exchange interactions [17], and the match of experimental and Heisenberg-model susceptibilities suggests that CuO could be classified as one dimensional [18]. However, this conclusion lacks a microscopic foundation, and the existence of a dominant interaction along the AF alignment is not obvious at all from the structural viewpoint, since the Cu-Cu distance parallel to the AF alignment (3.74 Å) is 20% larger than the Cu-Cu distance along the FM chains (3.17 Å).

To our knowledge, no explanation of this phenomenon based on a detailed chemical picture has been attempted so far. This explanation is, indeed, the main purpose of our work. We have performed pseudo-*SIC* calculations using ultrasoft pseudopotentials [19] with 30 Ryd cutoff energy and $6 \times 6 \times 6$ special k-point grids for total energy calculations; 250 special k-points and linear tetrahedron interpolation method for density of states (DOS) calculation. For the observed AF_z ordering we obtain structural parameters in good agreement with the experimental values (within 1%). However, in order to compare in an unbiased way the energies of different magnetic phases we assume the experimental structure for each phase.

The basic difference between LSDA and pseudo-*SIC* results can be understood from the sketch of the Cu^{2+} monoclinic crystal field splitting in Fig. 3 (left panel). Since the LSDA potential only depends on the total magnetization density $m(\mathbf{r})$ (very small in this case), a spin-polarized solution cannot be sustained and the self-consistency heads towards a metallic, nearly diamagnetic [20] ground state, where the Fermi energy E_F cuts the d_{z^2} antibonding doublet. On the other hand, pseudo-*SIC* depends [5] on the average magnetization of each individual
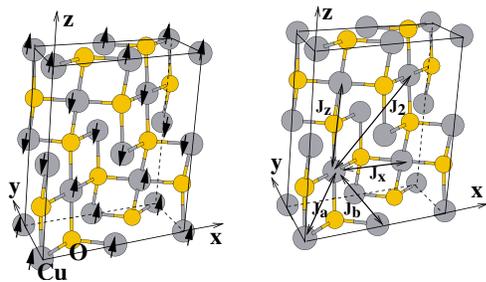
orbital, so that the self-consistency process reaches a spin-polarized ground state, with the d_{z^2} doublet split into majority (occupied) and minority (empty) contributions, of which only the former (being occupied) is descreened by its self-interaction correction. The magnitude of the correction ($\Delta_{d_{z^2}}^{\mathrm{SIC}}$ in Fig. 3) depends on the occupation and localization degree of each orbital.

The orbital-resolved DOS calculated within pseudo-*SIC* (Fig. 3, right) makes quantitative the concepts just exposed. The d_{z^2} spin splitting of 10 eV induces the formation of Cu magnetic moments of $0.72\mu_B$, remarkably close to the experimental value $0.68\mu_B$ [17]. As sketched in Fig. 3, the majority d_{z^2} states are at the bottom of the d band manifold. The d_{z^2} state, therefore, undergoes a much larger down-shift than the other majority d states. This is consistent with the fact that the Cu-O-Cu path is longer and more stretched out along z than along x.

Figure 4 shows the calculated magnetization density isosurface. On each Cu a d_{z^2}-shaped density, pointing towards the on-top O and forming the highlighted Cu-O-Cu vertical segments, is visible, while the planar lobes of the d_{z^2} orbitals point towards the two closest in-plane O forming planar Cu-O-Cu chains. (Notice that a residual magnetization is present on the O sites as well.) Thus, two non-vanishing Cu-O hybridizations, involving Cu d_{z^2} and O p orbitals, rule the magnetic ordering: a d_{z^2}-$p_z\sigma$ interaction, mainly responsible for the vertical AF alignment, and the d_{z^2}-(p_x, p_y) interaction which produces in-plane Cu-O FM chains and induces a non-negligible $\sim 0.1\mu_B$ magnetic moment on the oxygens.

Figure 5 shows the calculated band energies. The fundamental band gap opens between the 4 minority bands of mainly d_{z^2} character, and the valence band top, largely formed by oxygen bands. Thus, in agreement with the experiments, CuO is described as a charge-transfer insulator. The calculated energy gap $E_{\mathrm{gap}} = 2.2$ eV overestimates the reported experimental value 1.7 eV. This discrepancy might be due to a slight overestimation of the d band down-shift operated by the pseudo-*SIC*.

FIG. 2 (color online).   Unit cell of monoclinic CuO. In the left panel the arrows show the Cu magnetic moment orientation within the stable AF_z ordering. In the right panel the inequivalent exchange-interaction parameters are labeled.
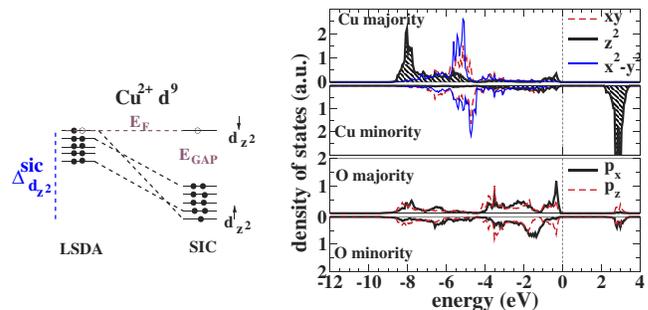
FIG. 3 (color online).   Left panel: monoclinic field splitting for Cu^{2+} ion within LSDA and pseudo-*SIC*. Right panel: orbital-resolved DOS of CuO in the AF_z phase calculated with pseudo-*SIC*.
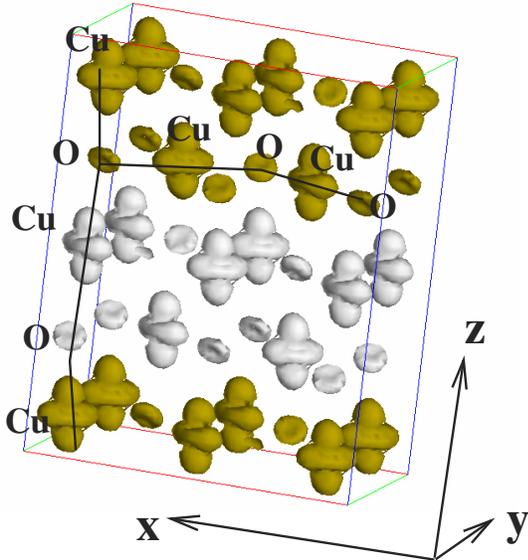
FIG. 4 (color online). Isosurfaces of magnetization density [green (gray in grayscale): spin-up; white: spin-down]. A d_z^2-shaped magnetization is centered on each Cu. A small, planar magnetization is also visible on the O sites. Solid lines highlight AF (vertical) and FM (horizontal) Cu-O chains

With these results at hand, a chemical picture relating structure, orbital, and magnetic ordering naturally arises. We start from a negatively ionized $Cu^{1+}O^{2-}$ system, that is cubic and diamagnetic. Then, neutral $Cu^{2+}O^{2-}$ is obtained by extracting one electron from the highest antibonding d state. This metallic configuration is stabilized by both monoclinic (Jahn-Teller) distortions and spin polarization: the (small) monoclinic field splits up the five d orbitals, the highest of whom is further split in up and down contributions, thus forming local magnetic moments on Cu and opening the energy gap. Also, the angle β (see Fig. 1) increases from its 90° cubic value and the internal parameter u (which equals $1/4$ in tetrahedral coordination)
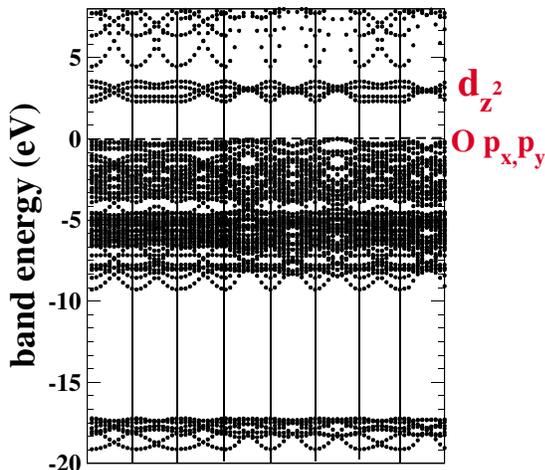
FIG. 5 (color online). Band structure of CuO in the AF_z phase.

changes so that the Cu-Cu distance along z increases, and the largest antibonding contribution, due to the overlap of majority d_{z^2} states, decreases. This in turn affects the magnetic ordering, since the Cu-O-Cu segments along z have now angles of 145° and, according to the GKA rules, must be AF being much larger than 90°. On the other hand, upon distortion the Cu-O-Cu angles along x (~109°) remain almost unchanged from the ideal tetrahedral values of 109.5°. Thus, we can understand the occurrence of the AF_z ordering as a consequence of the structural stabilization produced by the z-parallel Cu-O-Cu stretching. According to our calculations, the monoclinic distortion furnishes a 0.51 eV/formula unit energy gain over the ideal cubic structure (with $u = 1/4$ and $a = 2b = c$) within the same AF_z ordering.

The AF_z phase is reached in a self-consistent calculation starting from trial Cu magnetic moments oriented according to AF_z ordering. In order to prove that AF_z is the theoretical ground state and not a local minimum, we calculated (Table I) the energy of all possible AF and FM configurations within the 8-formula units cell. In all cases, we find stable solutions and, quite remarkably, the lowest-energy phase is the observed AF_z: all others can be interpreted as low-energy spin excitations. The lowest excitation (FM_x) corresponds to a triplet state (in agreement with experiments [17]) obtained by flipping spins on a single Cu-Cu chain parallel to x.

Further, we can extract the exchange-interaction parameters of the Heisenberg Hamiltonian $H_H = -\Sigma_{\alpha,ij} J_{\alpha,ij} \vec{S}_i \cdot \vec{S}_j$, $\alpha = x, y, z$) from the calculated energies. Clearly, we expect a negative (i.e., AF) exchange interaction along z. However, a single parameter is not sufficient to rationalize the whole spin-excitation energy spectra, since other configurations besides AF_z (e.g., AF_{101}, $AF_{\bar{1}01}$, FM_x) have AF coupling along z but very different energies. The J's reported in Table II confirm that CuO is strongly anisotropic and far from being a one-dimensional system. J_z is largest as it is due to the only σ-like interaction, i.e., Cu-O-Cu $d_z^2 p_z \sigma$.

The second-largest interaction, J_x, connects Cu atoms through in-plane Cu-O-Cu segments with $\theta = 108.91°$, it is FM, and nearly half of J_z in magnitude. Indeed, the in-plane d_{z^2}-p_z interactions are vanishing by symmetry, while

TABLE I. Energies (in meV/formula unit) of all possible spin orderings within the 8-fomula units cell. AF configurations are built by FM planes with alternating spin, compensating each other along the labeled direction. FM_1 is obtained from FM upon flipping a single Cu spin, FM_x and FM_z after flipping the spins of a single Cu chain parallel to x and z, respectively. All values are relative to the energy of the FM phase.

AF_x	AF_y	AF_z	AF_{101}	$AF_{\bar{1}01}$	FM_1	FM_x	FM_z
3.5	15	−26	0.3	−5	−2.6	−9.2	5.6

TABLE II. Exchange-interaction parameters J in meV (the labels refer to the right panel of Fig. 2), angles θ, and lengths d (Å) of corresponding Cu-O-Cu segments.

	J_a	J_b	J_x	J_z	J_2
	8	11.6	20.4	-38.4	-14
θ	95.71°	104.02°	108.91°	145.81°	
d (Å)	3.91	3.91	3.90	3.92	

the dominant contribution consists of the virtual transfer of 2 electrons from different (one p_x and one p_y) oxygen orbitals towards the two adjacent Cu: this leaves the bridging O doubly spin polarized, and provides a FM Hund's-rule exchange contribution. Of course, this process does not contribute to J_z since $d_{z^2}p_x$ and $d_{z^2}p_y$ hoppings are zero by symmetry for vertical Cu-O-Cu segments.

J_a and J_b have θ close to 90°, thus the AF contributions are suppressed. Both are smaller in magnitude than J_x since the FM mechanism based on double electron hopping from different oxygen orbitals is also suppressed (by symmetry, it is only possible to have Hund coupling between either p_x-p_z or p_y-p_z polarized orbitals, but p_z polarization is strongly adversed by J_z). Furthermore, we also find a remarkable AF second-neighbor interaction (J_2), which increases the stability of AF$_z$ ordering over the AF$_{101}$ and AF$_{\bar{1}01}$ having FM second-neighbor alignment. We note finally that assuming a one-dimensional, isotropic, first-neighbor model for CuO would imply a single J equal to 2 times the AF$_z$ energy, i.e., 52 meV. While this is consistent with the value $J = 67 \pm 20$ meV obtained by fitting experimental susceptibilities onto a one-dimensional single-band model [18], our results show that this J can be at best interpreted as a rough quantification of the exchange-interaction magnitude but it cannot include the complexity of the real CuO magnetic interactions.

In summary, we have shown that the complex interplay of structure, chemical bonding, and magnetic ordering in CuO can be understood in detail within the pseudo-*SIC* approach. Our results, consistent with the experiments, explain the observed magnetic ordering as the result of a monoclinic structural distortion lowering the energy of the antibonding, spin-polarized d_z^2 orbital. Since CuO is fully three dimensional, the analysis of low-energy spin excitation must include all the (anisotropic) first-neighbor and second-neighbor exchange interactions. These results outline the potential of our approach in performing realistic and practicable first-principles investigations on cuprates, such as, e.g., the study of structural, metal-insulating, and AF-paramagnetic phase transitions in high T$_c$ superconductors at varying oxygen doping, whose dominant microscopic mechanisms are still unknown.

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