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Jahn-Teller stabilization of magnetic and orbital ordering in rocksalt CuO

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Self-interaction-corrected local-density-functional calculations show that rocksalt-structure CuO spontaneously becomes insulating and magnetically ordered by tetragonal Jahn-Teller distortion of Cu-centered octahedra. The equilibrium structure is axially expanded by 9%, has a charge-transfer gap of 1.1 eV, and antiferromagnetic ordering-II with a $d_{x^2-y^2}$ spin-polarized hole and a Neél temperature of 530 K within the anisotropic Ising model.

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The monoxides of most $3d$ transition metals crystallize in rocksaltlike structures. They realize an insulating electronic spectrum removing spin-orbital degeneracies in the octahedral submanifolds t_g and e_g of the d shell by means of magnetic ordering and lattice distortions. Copper monoxide becomes a Mott-like charge-transfer insulating type-A antiferromagnet[1] via a less direct, though conceptually equivalent strategy: it adopts a relatively low-density monoclinic structure comprising distorted tetrahedral units (see the discussion in Ref. 2), called tenorite. Can CuO be stabilized in some close relative of the rocksalt structure ? Cubic rocksalt CuO would be a Pauli-paramagnetic metal. Given the $t_g^6 e_g^3$ orbital configuration of Cu^{2+}, spin-orbital degeneracy removal requires both magnetic order and symmetry-lowering structural distortions. The minimal distortion needed is the paradigmatic Jahn-Teller elongation of the Cu-centered octahedra along the z axis (rocksalt can be seen as made up of side-sharing octahedra). The symmetry of stable rocksaltlike CuO will therefore be no higher than tetragonal, with two lattice constants a (in-plane) and c (vertically).

The routes to gap opening and structure stabilization in CuO have enjoyed a revived interest after Siemons *et al.* recently grew[3] on cubic $SrTiO_3$ an ultrathin (∼15–20 Å) CuO film with apparently rocksaltlike structure. It thus appears timely to clarify theoretically the properties of the possible stable structures of bulk rocksaltlike CuO. In this Rapid Communication we report *ab initio* calculations on CuO done with the self-interaction-corrected local density-functional[4,5] (pSIC) method.[6,7] This fully *ab initio* parameter-free technique, as shown and discussed in detail elsewhere,[5,8] treats accurately the delicate chemistry of divalent Cu in cuprates, which are instead unapproachable by standard methods such as local-density approximation (LDA) or generalized gradient approximation (GGA). (Indeed, we have verified that LDA invariably produces a nonmagnetic metallic rocksalt CuO, as in the case of tenorite CuO.[2])

In Fig. 1 we report the energy vs c/a of tetragonal-rocksalt CuO in the nonmagnetic, ferromagnetic (FM), and four different antiferromagnetic (AF) ordering states, at the lattice constant $a=3.905$ Å of the $SrTiO_3$ substrate (see also below). In this structure, Cu atoms sit on an fcc lattice slightly elongated along the Cartesian z axis, and their spin arrangement defines the magnetic ordering. The AF phases we consider are AF-A, AF-G, AF-4, and AF-II. While these are only some of the many possible spin arrangements on this lattice, they suffice to calculate the independent magnetic couplings; also, by analogy with other monoxides, they are likely to capture the essential physics. AF-A is made of ferromagnetic planes stacked antiferromagnetically in pairs (similarly to tenorite) along z; it is barely metallic at all c/a's, with a single band dipping below the Fermi level in a small region of the Brillouin zone. AF-G is fully antiferromagnetic (and equivalent to two interpenetrating ferromagnetic cubic lattices), and has a tiny indirect gap over most of the c/a range. The last two, AF-II and AF-4, compete closely for stability. The lowest-energy structure in Fig. 1 is AF-II, typical of other transition-metal monoxides. It consists of z-, AF-stacked planes each built up of (110)-oriented ferromagnetic Cu rows arranged antiferromagnetically in the $(1\bar{1}0)$ direction (see further discussion below). This phase has a gap of 1.1 eV at the absolute structural-energy minimum. The AF-4 structure is very similar (see below) and very close in energy to AF-II. The topmost curve in Fig. 1 is the nonmagnetic metallic state, with an equilibrium c/a of 1 and degenerate e_g states. The tenorite structure studied in Ref. 2 is as expected energetically favored over all the present structures.

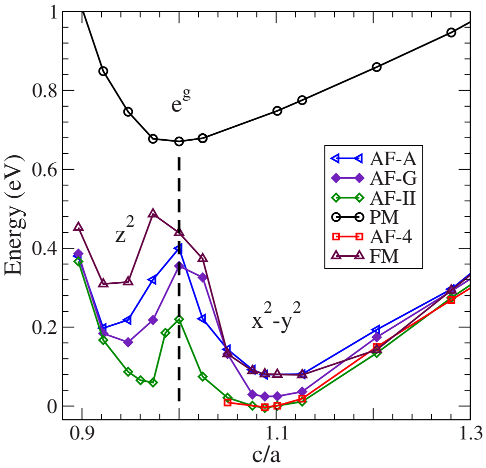

FIG. 1. (Color online) Energy per formula unit vs c/a for tetragonally distorted CuO, in-plane lattice constant $a=3.905$ Å. The energy zero is the lowest structure, AF-II at $c/a=1.09$. In the regions labeled "z^2" and "x^2-y^2," the magnetic hole has d_{z^2} and $d_{x^2-y^2}$ character respectively. The barrier between the two minima corresponds to degenerate e_g states.

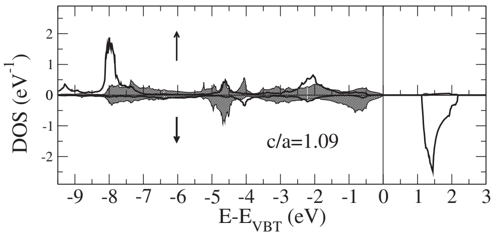

FIG. 2. Density of states of CuO projected on Cu e_g orbitals at the axially expanded minimum. Energy zero is the valence-band top. Thick solid line: $d_{x^2-y^2}$; thin solid line, shaded curve: d_{z^2}. The antiferromagnetically split Cu hole is almost pure $d_{x^2-y^2}$. The spin splitting of this state, 9.5 eV, is a measure of the effective on-site interaction U.

The energetics shows that the cubic nonmagnet (or Pauli paramagnet) collapses spontaneously into tetragonally distorted spin-polarized structures. The magnetic states have two distinct minima (Fig. 1), one metastable at roughly $c/a=0.97$ (vertical compression $\sim 3\%$), and one stable at $c/a=1.09$, corresponding to a vertical expansion of 9%. The c/a compression or elongation stems entirely from a Jahn-Teller distortion of the Cu-centered octahedron. The two minima are separated by a sharp maximum near $c/a=1$, related to the unresolved degeneracy of the partially occupied e_g doublet. In each of the two minima, the degeneracy is broken in favor of one of the e_g orbitals.

Examining the density of states (DOS) projected on Cu e_g orbitals for AF-II at $c/a=1.09$ in Fig. 2, we see that the empty minority state on Cu has essentially pure $d_{x^2-y^2}$ character; i.e., there is a $d_{x^2-y^2}$ magnetic orbital ordering at the absolute structural-energy minimum. Instead, the DOS in the metastable vertically compressed minimum in Fig. 3 shows that the polarized hole has d_{z^2} character, and hence a d_{z^2} magnetic orbital ordering. The gap increases monotonically from about 0.2 eV at $c/a=0.96$ to 2 eV at $c/a=1.35$. In the AF-II structure at the equilibrium $c/a=1.09$, the gap is 1.1 eV. It opens between mostly O p valence and purely Cu d empty states, which qualifies this variant of CuO as a charge-transfer Mott insulator. The calculated Cu magnetic moment in the AF-II structure is about $0.6\mu_B$ at both structural minima, quite in line with the moments usually found computationally in cuprates.[8]

Our main structural prediction is that c/a elongates by nearly 10%, a sizable Jahn-Teller effect by any standard. However, a c/a of over 1.35, i.e., a 35% expansion, has been inferred from diffraction measurements.[3] We opine that this is a strikingly, perhaps unreasonably, large number. The argument[3] that the volume per formula unit of elongated rocksalt at $c/a=1.35$ would be the same as in tenorite is hardly compelling. The volumes of the cubic nonmagnetic and polarized elongated structure (59 and 65 Å^3 per formula, respectively) are both far from the 80 Å^3 per formula of tenorite. The latter, however, is an open structure with locally tetrahedral coordination that naturally has a sizably larger specific volume than the close-packed octahedral rocksalt; this is similar, e.g., to Si in the diamond structure having a 20% larger volume per atom than in close-packed hcp or fcc.[9] A more robust proxy of bonding behavior in the various structures are Cu(2+)−O bond lengths. In cuprates, the latter cluster around 1.95−2 Å, and a Cu-O bond length of 2.65 Å as implied by experiment is quite out of the ordinary. To quote a fairly extreme example, in $\mathrm{YBa_2Cu_3O_7}$ (YBCO), the only sizably anomalous bond length is apical O to in-plane Cu at 2.25 Å, an elongation originating from a dramatic apical distortion of the Cu-O pyramid with basal face on Cu-O planes, due to chain Cu's pulling apical oxygen as close as 1.80 Å. (We stress that our considerations apply to Cu(2+): trivalent Cu can indeed establish Cu-O bonds as long as 2.75 Å. However, mixed valence is not expected in bulk CuO.)

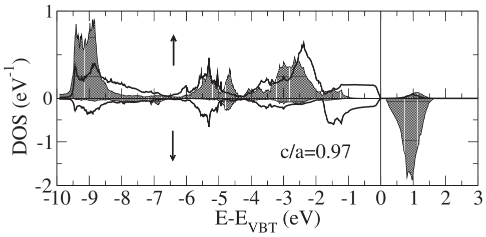

FIG. 3. Density of states of CuO projected on Cu e_g orbitals at the axially compressed minimum. Energy zero is the valence-band top. Thick solid line: $d_{x^2-y^2}$; thin solid line, shaded curve: d_{z^2}. The antiferromagnetically split Cu hole is almost pure d_{z^2}. The spin splitting is similar to that in Fig. 2.

Since in Fig. 1 the in-plane lattice constant is that of $\mathrm{SrTiO_3}$ substrate as in experiment, the Jahn-Teller vertical elongation is coupled to a lateral constraint. We estimated that the minimum energy for *free-standing* AF-II CuO in the expanded basin is at $(a,c)=(3.79,4.30)$ Å vs the epiconstrained $(a,c)=(3.905,4.25)$ Å. (In passing, this suggests e.g. $\mathrm{LaAlO_3}$, $a=3.79$ Å, as a substrate for CuO growth.) The vertical distortion is only slightly larger in the free-standing case, with comparable Cu-O bond lengths of 2.15 Å (free-standing) vs 2.125 Å (epitaxial), both very far from 2.65 Å. (We also have searched for off-plane distortions and buckling in the various structures, but found none.) Our present results, therefore, are circumstantial evidence that tetragonal-rocksalt CuO should have a bulk c/a closer to 1.1 than to the 1.35 reported so far experimentally for films.[3] The latter c/a value might be due to surface and interface effects, given that the films in question are ultrathin.

We now discuss magnetic couplings and ordering temperatures, motivated by the suggestion[3] that CuO in the rocksalt structure may have a Neél temperature T_N around 900 K, much larger than all other monoxides and than tenorite CuO. The lowest-energy AF-II structure can be seen as two interpenetrating AF simple-cubic sublattices, as shown in Fig. 4. There are two independent magnetic couplings in the basal plane, and two more in the vertical planes. (This holds also for AF-4: the differences with AF-II are schematized in Fig. 5.) The couplings within each sublattice ($J_\parallel$ in the basal plane and $J_\perp$ along the c axis) originate from O-mediated superexchange between Cu's that are second neighbors on the full lattice. The two sublattices are coupled by the "diagonal" terms $J_{d\parallel}$ in the basal plane and $J_{d\perp}$ in the vertical planes. As easily seen by inspection, in the expression of the magnetic energy for AF-II the terms involving diagonal J's cancel out, which cures the apparent frustration in this struc-

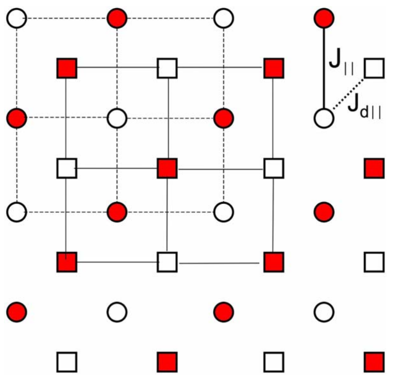

FIG. 4. (Color online) Schematic basal (xy)-plane view of the AF-II (or equivalently AF-4) structure. Filled and empty symbols indicate up or down spin. Square and circles are Cu atoms belonging to the two cubic AF sublattices discussed in the text. The intra sublattice AF coupling is named $J_\parallel$ and the intersublattice coupling is named $J_{d\parallel}$. Note that the apparent frustration is avoided in this structure because the contributions involving $J_{d\parallel}$ cancel. The vertical xz plane is obviously equivalent upon exchange of ∥ by ⊥, and allowance for the different numerical value of the J's. Oxygens (not drawn) sit at the crossings of the two nets.

TABLE I. In-plane (∥) and vertical (⊥) magnetic couplings (meV) and Neél temperatures (K) for Jahn-Teller-distorted CuO in the AF-II structure.

$J_\parallel$	$J_{d\parallel}$	$J_\perp$	$J_{d\perp}$
−28.4	−27.3	−5.6	2.5
T_N(Ising)		T_N(Weiss)	
plain	rescaled	plain	rescaled
530	300	725	410

ture. Therefore, the relevant ordering temperature can be estimated for each sublattice separately. As shown below, the intralattice couplings are AF and anisotropic (one J is one fifth of the other). Thus each sublattice can be mapped onto an anisotropic Ising model (three-dimensional, simple-cubic, antiferromagnetic).

The coupling parameters are calculated from the total energies of the various magnetic phases as

$$J_\parallel = (2E_{\mathrm{AF\ II}} - E_{\mathrm{AF\ G}} - E_{\mathrm{AF\ A}})/2,$$

$$J_\perp = E_{\mathrm{AF\ II}} - E_{\mathrm{AF\ 4}},$$

$$J_{d\parallel} = (E_{\mathrm{AF\ G}} - E_{\mathrm{AF\ A}})/2,$$

$$J_{d\perp} = (E_{\mathrm{AF\ 4}} + E_{\mathrm{AF\ A}} - E_{\mathrm{FM}} - E_{\mathrm{AF\ II}})/2. \qquad (1)$$

The calculated parameters are $J_\parallel = -28.4$ meV, $J_{d\parallel} = -27.3$ meV, $J_\perp = -5.6$ meV, and $J_{d\perp} = 2.5$ meV. The anisotropy ratio is $J_\perp / J_\parallel = 0.197$, i.e., as anticipated the system is strongly two dimensional in terms of magnetic interaction.

A simple estimate of the Néel temperature can be obtained[11] by a modified Weiss formula: we find $T_N = 725$ K for AF-II. Applying Anderson's rescaling[11,14] this estimate drops to 410 K. Since the present system is quite anisotropic, a formula born of isotropic classical models may not apply. We therefore employ results for the anisotropic Ising model. The critical temperature is a maximum in the isotropic case (1500 K for our calculated maximum J), and drops[12] with increasing anisotropy, as one would intuitively expect. From renormalization-group data[13] on the anisotropy dependence of the critical temperature, we infer a Néel temperature of 530 K at the calculated ratio $J_\perp / J_\parallel \simeq 0.2$. Upon Anderson scaling, T_N drops to 300 K. The data are collected in Table I. It appears that the present estimates (except to some extent for the unscaled Weiss formula) do not confirm the suggestion about a Neél temperature of rocksalt CuO much larger than in other transition-metal oxides. This is clearly expected given the strong anisotropy of in-plane and vertical coupling, and the weakness of the latter.

In Fig. 6 we compare our calculated valence DOS with the UPS peak positions.[3] The general shape and energy positions (see Ref. 3) are in fair, though not especially striking

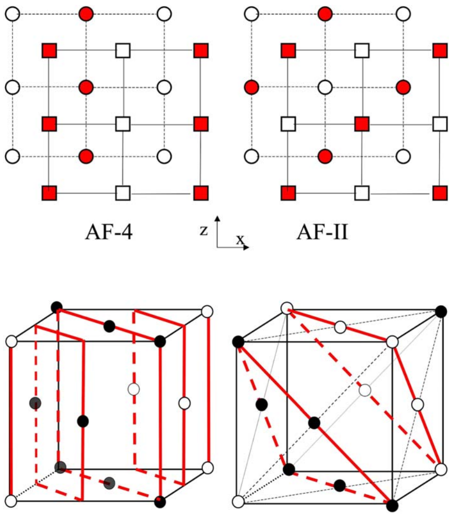

FIG. 5. (Color online) Top: stacking sequence of the AF-II (right) and AF-4 structures (left) viewed in the vertical (010) plane the c axis being (001)). Bottom: alternate view of AF-II (right) and AF-4 (left) as, respectively, (111)-oriented monolayer and (110)-oriented bilayer AF-A structures. Filled and empty symbols are up and down Cu's. Oxygens are not shown.

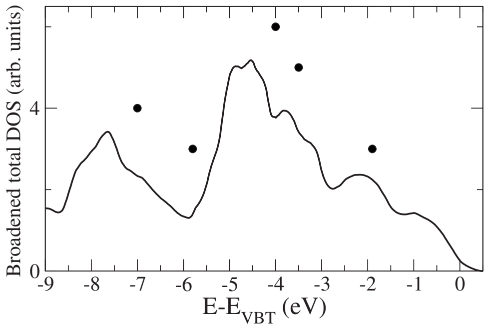

FIG. 6. Valence density of states compared with UPS peak positions. The DOS is broadened by a running average procedure.

agreement with experiment. On the other hand, if our conjecture about the possible interface and surface-induced expansion of the measured sample is correct, our DOS and the UPS spectrum should not necessarily agree, and this imperfect matching is not too disturbing.

In a recent paper Grant[10] studied rocksalt CuO using LDA+U. He finds that both a substantial U (6 eV, which e.g., we also found to be the minimal value needed to open a gap in $YBa_2Cu_3O_6$) and a tetragonal distortion are needed to open a gap in the spectrum. He investigated only the expanded-c/a basin of the magnetic phase, finding a shallow structural minimum at about $c/a=1.2$, somewhat closer to our value than to experiment. The vertical Cu-O bonds of 2.35 Å are reasonable, though still somewhat large. The value of U suggested by our calculations (over 9 eV) is larger than that used by Grant: whether and how much U affects structure is an open question.

In summary, parameter-free *ab initio* self-interaction corrected density-functional calculations show that metallic rocksalt CuO stabilizes by Jahn-Teller distortion at $c/a=1.09$ in an AF-II magnetic arrangement with $d_{x^2-y^2}$ orbital ordering and a charge-transfer gap of 1.1 eV. The Jahn-Teller distortion of the Cu-centered octahedra is a sizable 10%. Given our results, and other typical Cu-O bond lengths in cuprates, we suggest the 35% expansion reported in experiment may be due to interface and surface effects. We estimate relatively low Neél temperatures (between 300 by Anderson-rescaled anisotropic Ising model, and 750 K by unrescaled Weiss formula) due to the strong anisotropy of magnetic couplings; hence, we do not support the suggestion of high Neél temperature in tetragonal-rocksalt CuO.

Note added in proof. It has been brought to our attention that a hybrid-functional calculation on tetragonal CuO has been published by Chen *et al.*[15]

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