Electronic properties of rocksalt copper monoxide: A proxy structure for high temperature superconductivity

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Abstract. Cubic rocksalt copper monoxide, in contrast to its lighter transition metal neighbours, does not exist in nature nor has it yet been successfully synthesized. Nonetheless, its numerical study as a structurally much simpler proxy for the layered cuprate perovskites may prove useful in probing the source of high temperature superconductivity in the latter family of compounds. Here we report such a study employing density functional theory (DFT) abetted by the local density approximation including cation on-site Hubbard interactions (LDA+U). Rather surprisingly, we find that unlike oxides of the light transition metals, cubic CuO remains metallic for all physically reasonable values of U and does not result in a Mott-Hubbard induced charge transfer insulator as might be expected, and, in fact, displays a Fermi surface with clearly nesting tendencies. Preliminary calculations of the net dimensionless electron-phonon coupling constant, λ, yield values in the range 0.6 - 0.7 similar to those found for the superconducting fullerenes and magnesium diboride. On the other hand, we do find as we gradually introduce a tetragonal distortion away from pure cubic symmetry that a charge-transfer insulator emerges for values of U ~ 5 eV and c/a ~ 1.3 in agreement with recent experimental data on forced-epitaxial growth of 2-4 ML thick films of tetragonal rocksalt CuO. We preliminarily conclude from these computational studies that high temperature superconductivity in the copper oxide compounds is at least initially mediated by Jahn-Teller driven electron-phonon coupling as originally suggested by Bednorz and Mueller.

1. Introduction

Twenty-two years after the discovery of high temperature superconductivity in the copper oxide perovskites, its origin and mechanism remain unclear and controversial. In this paper we approach this issue with a novel concept, i.e., the idea of examining with computational chemistry techniques, a proxy structure that contains what we believe to be the essential physical nature of these materials. The proxy we choose is rocksalt copper monoxide to which we apply density functional theory abetted by a Hubbard modification to the local density approximation.

Rocksalt copper oxide is not found in nature, nor, to the knowledge of the author, have various attempts at its synthesis proved successful. One might have expected it to be the terminal compound

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in the series of the heavy fourth row (Mn, Fe, Co, Ni, Cu) transition metal oxides. Instead what one does find is the mineral tenorite, a highly distorted monoclinc crystalline form with four distinct CuO molecules per unit cell. Immediately one recalls the original suggestion by Bednorz and Mueller [1], following on Chakravarty [2], Hoech [3] and others, that a highly symmetric divalent copper monoxide structure would likely succumb to a Jahn-Teller distortion producing a strong electron-phonon interaction which might mediate superconductivity. Thus one is encouraged to explore ideally cubic rocksalt CuO (c-rs-CuO) as well as, to mimic Jahn-Teller effects, tetragonally distorted rocksalt CuO (t-rs-CuO), as structural proxies in the hope that their study may more clearly elucidate the fundamental driving factors underlying high temperature superconductivity.

2. Methodology

We start with the tacit assumption that rs-CuO, like its four immediate predecessors, would be an antiferromagnetic charge transfer insulator resulting from the splitting off to a separate empty conduction band the unoccupied states of an otherwise partially filled (and therefore conducting) 3d valence manifold, mitigated by on-site coulomb repulsion of otherwise Pauli-allowed single-state opposing spin pairs. It is well known that, if it were not for this "Hubbard U" interaction, single particle band theory predicts metallic behaviour for all "final five" 3d transition metal oxides. Thus we use as our computational probe for rs-CuO, the local-density-approximation plus Hubbard-U (LDA+U) modification to standard density functional theory (DFT) in order to properly take into account such coulomb correlation effects.

The particular implementation of DFT(LDA+U) we chose was the PWscf plane-wave-psuedopotential package available within the QUANTUM-ESPRESSO suite of codes [4]. We followed the general procedure used by Coccocioni and de Gironcoli [5] for FeO and NiO, taking as the primitive AF type II unit cell a rhombohedral structure containing two CuO molecules (one spin up, the other down), oriented along the (111) direction of the chemical unit cell. For the cubic lattice constant of c-rs-CuO, we selected 3.905 □, roughly double the average planar Cu-O distances in $La_2CuO_{4-\delta}$. Our Hubbard values ranged from 0 to 7.5 eV, covering what we consider all possibly reasonable values. We thoroughly tested the code against MnO, FeO, CoO, NiO and tenorite-CuO, obtaining metals for U = 0 and charge-transfer insulators of varying bandgaps otherwise, in general agreement with other published LDA+U calculations on these materials. More detailed discussion regarding our computational methods will be addressed in a future publication.

3. Results

3.1. Cubic Rocksalt Copper Monoxide (c-rs-CuO)

Our principal findings for c-rs-CuO are summarized in figures 1 - 4, the most profound being that c-rs-CuO is a metal for all values of U tested.

The left hand panels of figures 1 -2 depict the band structure and total and projected density of states for c-rs-CuO with U = 0. One sees immediately that the upper valence band electron density is shared roughly 2:1 at the Fermi level between Cu 3d and O 2p states, and the ground state is, as expected, itinerant. However, unlike its lighter cousins, c-rs-CuO remains metallic for an on-site repulsion energy U = 6 eV as shown in the right hand panels. Moreover, the proportion of charge sharing between d and p levels at E_F remains roughly the same, lending credence to the experimental observation that a portion of the holes that pair in the high-T_C cuprates reside on the oxygen anions. In fact, one sees that the main influence of Hubbard U is to "disentangle" and "move deeper" the Cu 3d levels of t_{2g} crystal field symmetry ~3 eV below E_F, rather than split into separate bands the higher lying e_g states near the Fermi level. All these observation are consistent with the assertion by Newns and Tsuei [6] that on-Cu site charge fluctuations may not play as important a role in mediating high temperature superconductivity as some models might infer.

Figures 3 and 4 display the Fermi surface of c-rs-CuO for U = 0. As seen from the top panels of figure 1, it is essentially that for U = 6 eV as well. The complexity of the surface morphology arises

from the numerous hole pockets and the Brillouin zone folding brought about by the doubly periodic AF type II unit cell. Note the large number of nearly commensurate planar surfaces especially apparent in

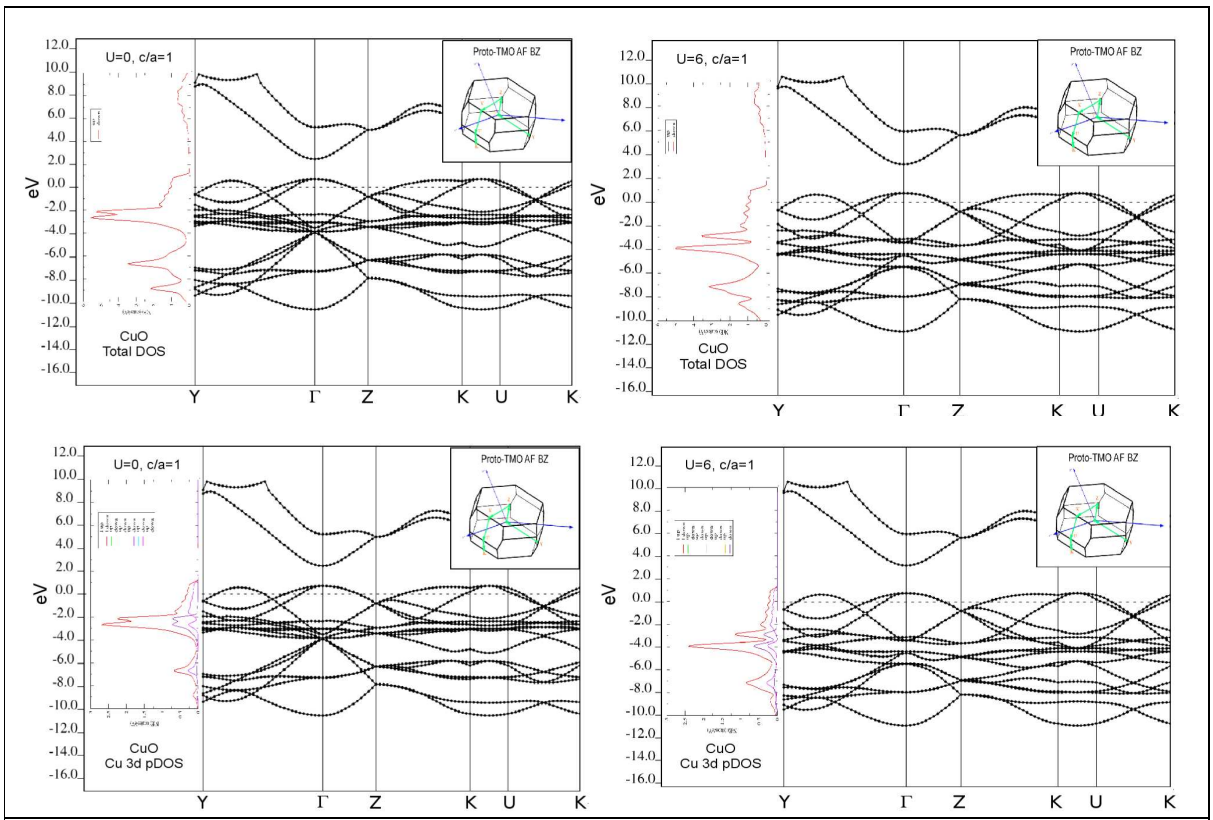

Figure 1. The band structure and density of states of cubic rocksalt CuO as a function of Hubbard U and Cu valence orbital decomposition. Note the generic TMO AF II Brillouin zone in the upper right hand corner of each panel. c/a = 1 for all panels. Upper Left: Total DOS(0 -6 /eV), U = 0. Upper Right: Total DOS(0 -6 /eV), U = 6. Lower Left: Cu 3d projected DOS(0 -3 /eV), U = 0. Lower Right: Cu 3d projected DOS(0 -3 /eV), U = 6.

figure 4. Such geometries provide ripe opportunities for nesting resulting in large electron-phonon coupling thus leading to Jahn-Teller instabilities…or superconductivity.

The code for computing electron-phonon interactions for spin-polarized systems explicitly is currently undergoing construction within the QUANTUM-ESPRESSO consortium. In the meantime, inasmuch as the fermiology of c-rs-CuO is practically independent of the magnitude of U, it is useful to consider a calculation of the e-p coupling for the chemical primitive cell contained a single CuO molecule. The relevant Fermi surface is shown in figure 5. Note that removing the AF II translational symmetry also removes much, but not all, of the nesting features of figures 3 and 4, which may in the end turn out to be critical to the magnitude of T_C, an issue we defer to when the spin-polarized e-p code is available.

The approach we use to compute the electron-phonon coupling follows the method used for niobium employing the QUANTUM-ESPRESSO programs by Wierzbowska, di Gironcoli and Gianozzi [8]. The details of our calculation will be published in a subsequent paper, but we stress that accurate calculations of electron-phonon coupling parameters requires a double-delta function integration over a dense net of electron and phonon k and q vectors, and access to significant computational resources. Our simple and highly symmetric c-rs-CuO proxy reduces the effort somewhat, and we used a 16×16×16 Monkhorst-Pack mesh for the electronic DOS, 8×8×8 for the

band structure and 4×4×4 for phonons, sufficient to approximate the dimensionless e-p coupling constant, $\lambda \sim 0.3$, for fcc aluminum. For c-rs-CuO, we find a range of $\lambda \sim 0.6 - 0.7$ depending

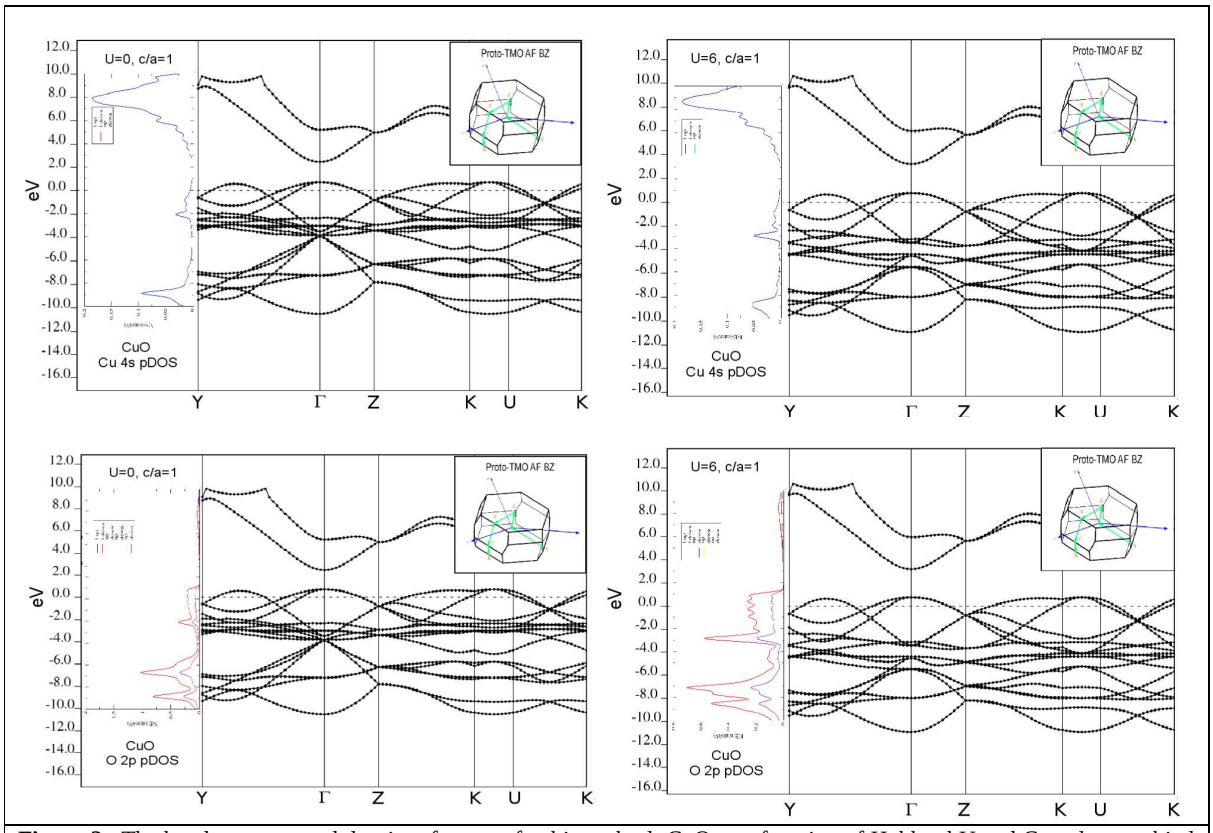

Figure 2. The band structure and density of states of cubic rocksalt CuO as a function of Hubbard U and Cu valence orbital decomposition broken down by non-d Cu orbital cation and O^{-2} anion ligands. c/a = 1 for all panels. Upper Left: Cu 4s projected DOS(0 - 0.2 /eV), U = 0. Upper Right: Cu 4s projected DOS(0 -0.2 /eV), U = 6. Lower Left: O 2p projected DOS(0 -0.25 /eV), U = 0. Lower Right: O 2p projected DOS(0 -0.8 /eV), U = 6.

on the gaussian smoothing constant used to effect the double-delta integration. These values are representative of those found for the superconducting fullerenes with T_c's ~ 16 -47 K, and "all phonon mode" values for MgB_2, $T_c \sim 40$ K. Figure 6 displays the frequency dependence of the Eliashberg kernel, $\alpha^2F(\omega)$, only for "all-modes." Its general shape and magnitude is consistent with our range of lambda obtained. We leave as a future exercise the exploration of individual modes to investigate whether a special circumstance exists, as in MgB_2, where a single branch dominates the electron-phonon spectral behaviour, as well as the calculation of a hypothetical tunneling spectrum.

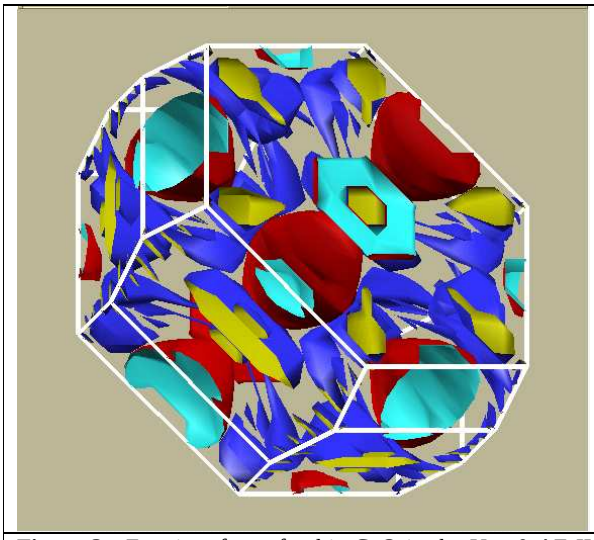

Figure 3. Fermi surface of cubic CuO in the U = 0 AF II primitive cell reciprocal lattice [7]

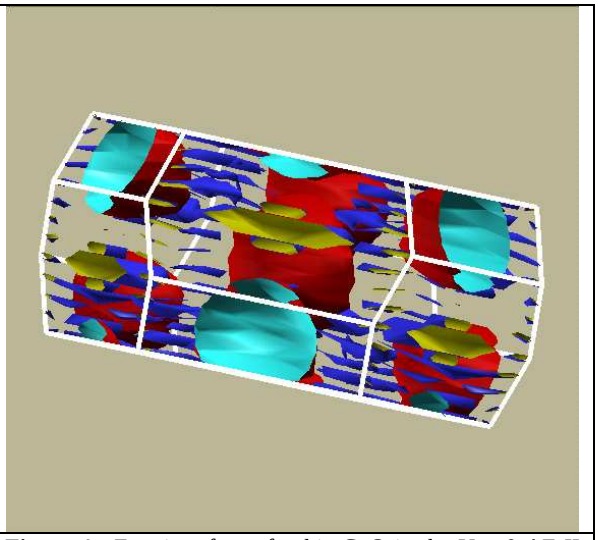

Figure 4. Fermi surface of cubic CuO in the U = 0 AF II primitive cell reciprocal lattice, oriented to display explicitly the nesting features of numerous "mini-sheets."

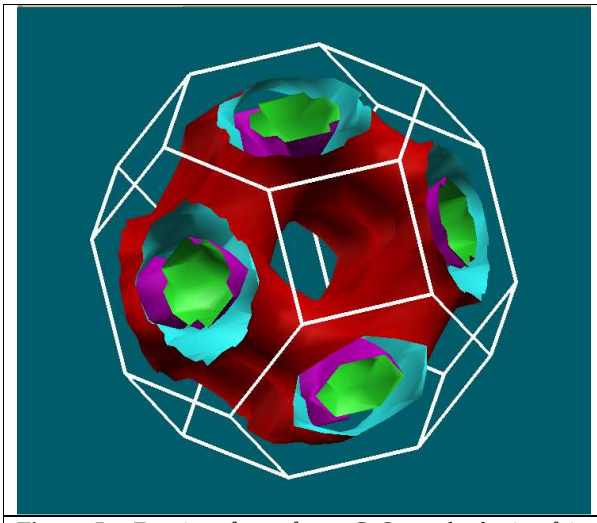

Figure 5. Fermi surface of c-rs-CuO on the basis of its simple non-antiferromagnetic chemical unit cell.

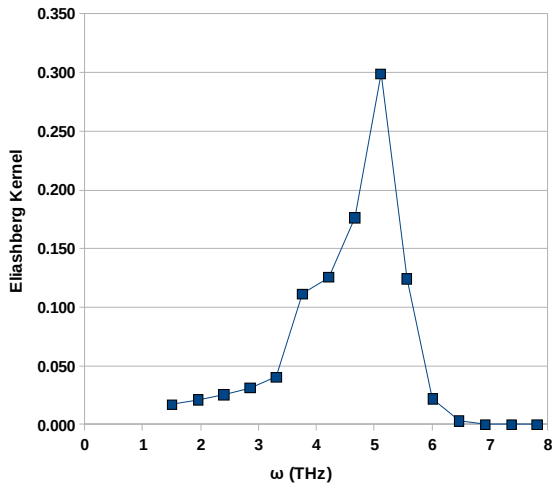

Figure 6. "All-modes" Eliashberg kernel, $\alpha^2F(\omega)$, for c-rs-CuO. Gaussian smoothing factor $\sigma = 0.04$.

3.2. Tetragonal Rocksalt Copper Monoxide (t-rs-CuO)

We next consider a straightforward mimicking of a Jahn-Teller distortion provided by a suitable tetragonal distortion of c-rs-CuO projected on the c-axis of an otherwise cubic unit cell. In fact, such a structure has recently been observed within 2-4 monolayer (ML) on forced-epitaxial films grown on strontium titanate (STO) substrates by Siemons, et al [9]. Employing x-ray photoemission diffraction methods (XPD), the authors were able to determine the lattice constants of these thin films to be a = 3.905 □ and c = 5.3 □, or a (rather large) distortion, c/a = 1.36. Figure 7 summarizes the band structures and DOS for these lattice parameters with U = 0 and U = 5 eV, respectively. It is seen for U = 0 and c/a as chosen, t-rs-CuO remains metallic as might be expected. However, one observes the onset of crystal field splitting of the Cu 3d eg states, and, for U = 5, these levels are pushed further apart resulting in a gap at EF, analogous to the behaviour found in the cubic rocksalt lighter transition

metal monoxides (see also the right hand panel of figure 10 which will be discussed further forthwith). Figure 8 shows clearly the "cooperation" between Jahn-Teller and Hubbard in creating the Mott-Hubbard charge transfer ground state in the undoped copper oxide perovskites. In fact, one can consider t-rs-CuO for 1 < c/a < 1.5 as a proxy for varying the doping levels of the former without having to resort to lanthanide-alkaline earth substitutions.

At present, the sole contact we have between our calculations on t-rs-CuO and experiment is provided in figure 9. Shown are the density-of-states for t-rs-CuO with c/a = 1.36 for U = 0, 5 and 7.5 eV with the inset depicting the HeI UPS spectra from 2-4 ML films of tetragonal rocksalt CuO grown by Siemons, et al., [9]. The highest intensity peak in both the computed DOS and intensities yielded from the samples derives from the 3d t2g manifold common to all the heavy rocksalt transition metal oxides. It is relatively clear that, given the inevitable broadening inherent in photoemission spectra, the best agreement is obtained for U = 5 eV calculation. Note

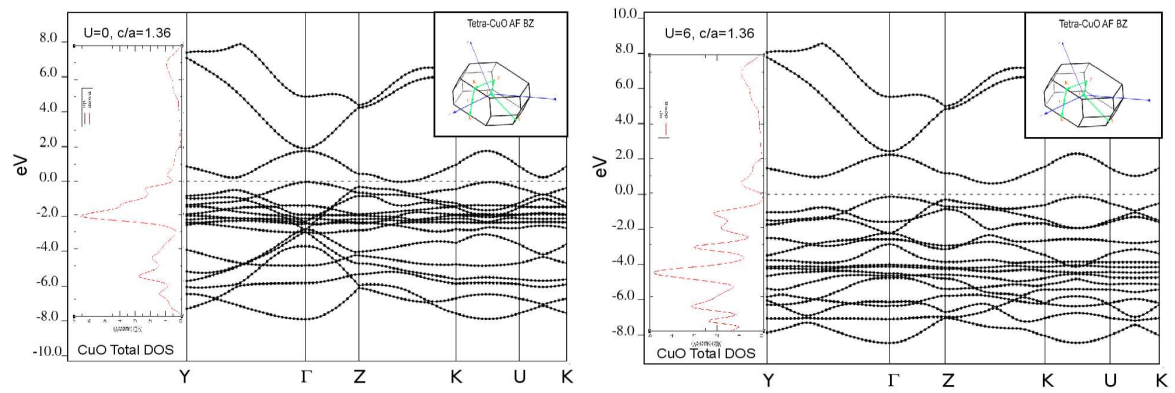

Figure 7. The band structure and density of states of tetragonal rocksalt CuO as a function of Hubbard U and Cu valence orbital decomposition broken down by non-d Cu orbital cation and O^{-2} anion ligands. c/a = 1.36 for both panels. Left: Cu 4s projected DOS, U = 0. Upper Right: Cu 4s projected DOS, U = 6.

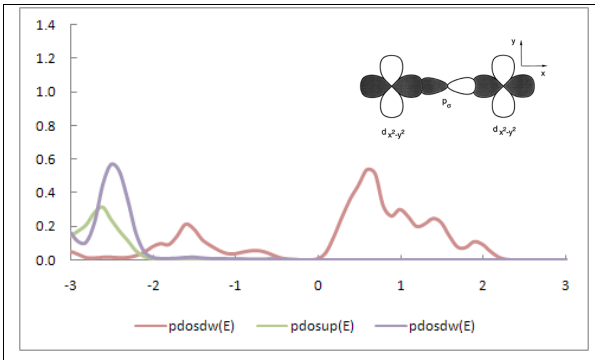

Figure 8. Projected DOS (0 – 1.4/eV) vs band energy scaled to EF of the uppermost eg states for t-rs-CuO, c/a = 1.36 (a = 3.905 □) showing clearly their separation and gap formation at U = 5 eV.

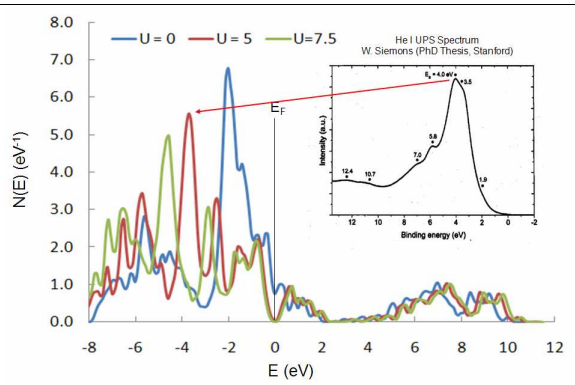

Figure 9. Comparison of N(E) of c/a = 1.36 t-rs-CuO for U = 0, 5 and 7.5 eV with HeI UPS spectra taken on 2-4 ML films [9]. The agreement is best nearest the -4 eV t_{2g} manifold for U = 5 eV,

that there is little evidence of a Fermi edge in the UPS data, and our calculations support this conclusion as well.

We also calculated the total DFT(LDA+U) ground state energy and density of states at the Fermi energy as a function of c/a between 1.0 and 1.5 for t-rf-CuO. The results are given in the left and right hand panels of figure 10, respectively. We note that the total energy approaches a minimum value, for

both U = 0 and 6, around c/a ~ 1.2, and, the density of states at the Fermi level dives toward zero as well. It should also be noted that c/a around 1.2 is also very close to 1.27, the ratio of the planar to apical Cu-O bond distance in $La_2CuO_{4-\delta}$.

Finally, in the hope of uncovering some possible evidence for electron-lattice instabilities that might arise for small tetragonal elongations in the range 1 < c/a < 1.1, given the ongoing development of electron-phonon coupling code accommodating spin-polarized states in QUANTUM-ESPRESSO, we carried out total energy calculations on a denser set than used for figure 10. To assure the least possible scatter in what turns out to be quite small differences in very large numbers, we used a Monkhorst-Pack net of 12×12×12 and an scf convergence value of < 10^{-9} Ry. Our results are contained in figure 11. We observe that there is a discernible "kink" around c/a ~ 1.048. Could this be a signature of "vibrational square" nonlinearities as suggested by Newns and Tsuei [6]?

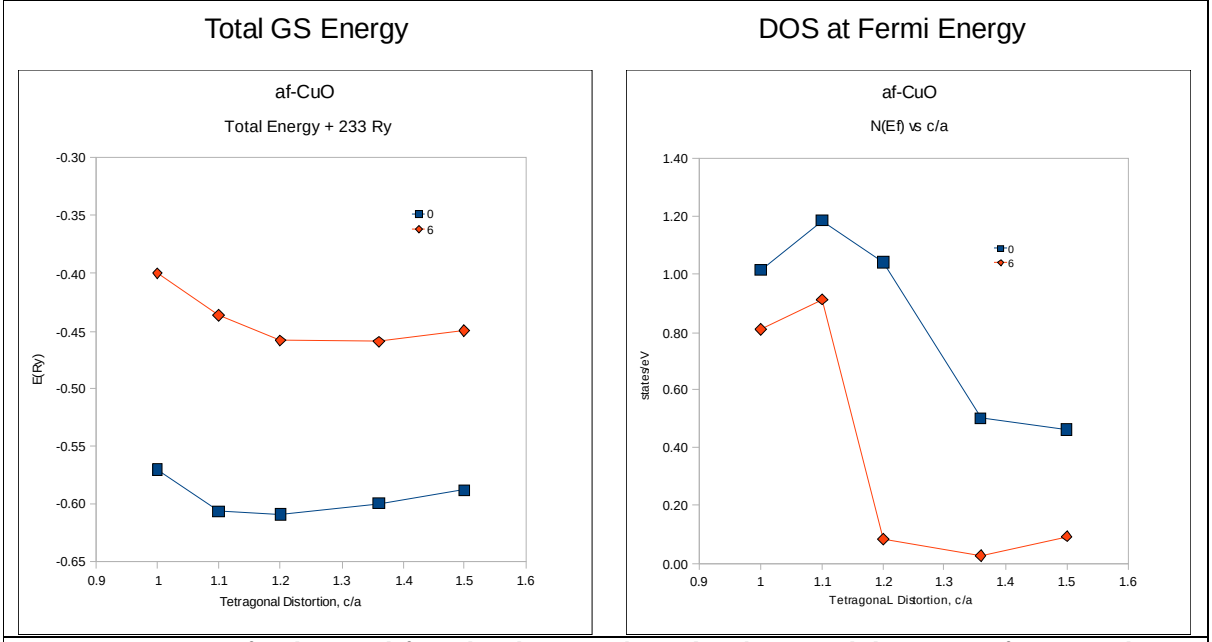

Figure 10. Variation of total energy (left panel) and $N(E_F)$ (right panel) with tetragonal elongation c/a for U = 0 and U = 6 eV. Note that the energy minimum is reasonably close to 1.27, approximately the ratio of the planar to apical Cu-O bond distance in $La_2CuO_{4-\delta}$. Note also that while at U = 0, t-rf-CuO remains metallic up to c/a = 1.5 (and probably higher), for U = 6 a gap begins to form at c/a = 1.2 as well (See figure 8).

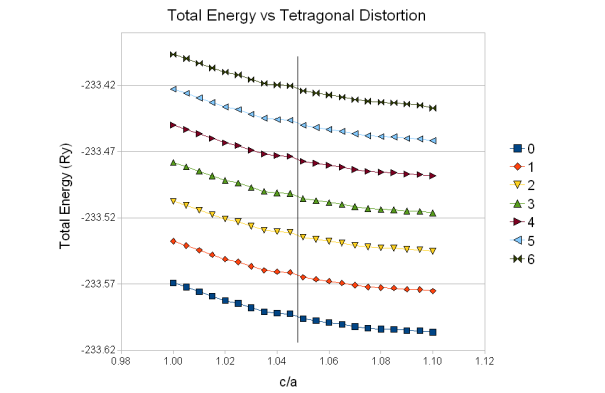

Figure 11. Total Energy (Ry) vs t-rs-CuO elongation factor, c/a (a = 3.905 □). The vertical line designates the onset of a "kink" in the total energy for c/a ~ 1.048.

4. Summary and Conclusions

To summarize:

- We have introduced the novel concept of "proxy materials" to aid elucidation of the underlying physics of more complex structures, using rocksalt copper monoxide as an initial example. We anticipate this approach can be extended to a number of hypothetical nano-configurations to investigate interesting properties prior to synthesis.
- We find cubic copper monoxide (c-rs-CuO) to be a metal for all physical values of Hubbard U contrary to "conventional" wisdom.
- c-rs-CuO is subject to strong Jahn-Teller distortions, in accord with the original notions of Bednorz and Mueller [1].
- A calculation of the dimensionless electron-phonon coupling constant, λ, suggests a T_C in the range 40 – 60 K is physical feasible for non-spin-polarized c-rs-CuO.
- Tetragonal rocksalt CuO (t-rs-CuO) with coulomb correlation included can provide an "self-doped" surrogate for the high temperature superconducting copper oxide perovskites.

For follow-up: A plethora of interesting questions and opportunities follow from the present study of the proxies c-rs-CuO and t-rs-CuO.

- When code is available, compute $\lambda = f(c/a, U)$ for t-rs-CuO.
- Then compute T_N, u*, BCS pre-factor and thenT_C.
- Look for evidence of anharmonic phonon interactions as suggested by Newns and Tsuei [6].
- Compute "low energy" spectral properties, e.g., interband transitions and raman scattering and Boltzmann transport coefficients as a function of c/a, or "doping."
- Estimate isotope effect.
- Calculate condensate symmetry.

5. Acknowledgements

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