Electronic Structure and Spectra of CuO

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(Dated: May 31, 2013)

PACS numbers: 71.27.+a,71.15.Mb,74.25.Jb,78.20.-e

We report the electronic structure of monoclinic CuO as obtained from first principles calculations by DFT + U method. In contrast to standard DFT calculations taking into account electronic correlations in DFT + U gave antiferromagnetic insulator with energy gap and magnetic moment values found to be in good agreement with experimental data. The electronic states around Fermi level are formed by partially filled Cu 3d_{x^2−y^2} orbitals with significant admixture of O 2p states. Theoretical spectra were calculated using DFT + U electronic structure and their comparison with experimental PES and optical spectra show very good agreement.

I. INTRODUCTION

The cupric oxide (CuO) system has been studied for decades both for fundamental understanding and applied reasons. It is generally recognized as the prototype material of a broad family of the strongly correlated (SC) oxides[1] Although the local environment of Cu in the Cu-O planes are strongly distorted, the planes share many commonalities to those thought to be responsible for superconductivity in the layered cuprate systems[2,3] A consequence of this, a good understanding of the electronic structure of CuO will play a key role in understanding and developing models for the normal state behavior of the high temperature superconducting cuprates. High-temperature superconductivity was discovered in the copper oxide perovskites as early as 1986[4,5] but its origin and mechanism are still under intense debate.

CuO is an exceptional member of the generally, rocksalt family as it deviates both structurally and electronically from others as one traverses the periodic table from MnO to CuO. Unlike other members of the 3d transition oxides (TMO) which crystallizes in the cubic rocksalt structure (with possible rhombohedral distortions)[6,7] Tenorite (CuO) crystallizes in the lower symmetry monoclinic (C_{2h}) crystal structure. Also, Unlike other antiferromagnetic (AFM) semiconductors, with known disordered paramagnetic character above the Néel temperature, CuO behaves as a 1D antiferromagnet[8] with strong antiferromagnetic ordering especially along the (101) direction prevailing even above the Néel temperature of 231 K. A 3D collinear antiferromagnetic order have been reported below 213 K[9] while between 213 K < T_N ≈ 231 K, it is reported to have a 3D non-collinear antiferromagnetic order.[11] Also, CuO has substantially lower than expected Néel temperature T_N ≈ 230 K, following a simple linear extrapolation of the trend of other TMOs across the periodic table. However, like other TMOs, CuO is an antiferromagnetic insulator[12,13,14]

Aside the fundamental importance of CuO in understanding the properties of high-temperature superconductivity, it has other important practical technological applications. CuO has found practical applications in areas such as gas sensor,[14,15] solar cells and photovoltaics,[15,16] catalysts,[17] varistors,[18] electrode in lithium ion batteries[19,20] and magnetic storage media.[21] Also, studies on CuO have shown strong dependence of its properties on quantum size effects[21,22] and has recently been shown to exhibit multiferroicity at T_c ~ 230 K.[23,24]

Experimentally, CuO is a monoclinic crystal structure with C2/c symmetry.[25,26] It has eight (8) formula units per magnetic unit cell. It is further reported to be a p-type semiconductor with band gap of 1.0 – 1.9 eV[14,21,27] and local moment per formula unit of ~ 0.7 µB.[10,11,28] There have been many theoretical computations utilizing density functional theory to study CuO.[29] These calculations rather predicted a nonmagnetic ground state with metallic character instead of the well-known semiconducting ground state. While the failures of these computations in obtaining the correct electronic properties of CuO should be understood by their intrinsic nature (inability to treat electron-electron interactions in the so-called correlated systems), recent improvements in first-principle theories based on density functional theory (DFT) plus screened Coulomb interaction (U) (DFT + U) as proposed, developed and applied by Anisimov et al.[12,13,14] has remedied this situation. While this method has been used to study the band structure of CuO (see for e.g., Refs [12,13,14]), we are not aware of any optical study of CuO utilizing this method.

As noted earlier, there have been many theoretical[12,13,14,15,16] and experimental studies[15,17,18,19,20,21,22,23,24,25,26,27,28,29] of CuO. The purpose of this paper is thus to present optical properties of CuO based on the modern band structure computations obtained with the potential functional of Anisimov et al.[13] This functional yields electronic properties of the strongly correlated systems in agreement with experiments.[12,13,14] in contrast to standard density functionals. Therefore, enables direct, quantitative comparisons of band struc-
tures and optical properties with experiment, without any adjustments, such as scaling the magnitude of the absorption or applying scissors operators to fix the gap. We extensively discuss the results in relation to experimental data. We hope that they will motivate future experimental investigations of the band structure of CuO particularly using optical measurements and photoemission.

The rest of this article is organized as follows. After this introduction in section I, the computational methods and details are given in section II. The results of our self-consistent calculations are presented and discussed in section III. We will then conclude in section IV.

II. METHOD AND COMPUTATIONAL DETAILS

One difficulty in the computation of material properties is that the band gaps and related properties of most materials are generally underestimated by the standard density functional theory (DFT) approximations. To avoid this, we utilized the density functional theory (DFT) plus the effective Coulomb interaction (U) (DFT + U) formalism using the general potential linearized augmented planewave (LAPW) method as implemented in the WIEN2k code. Unlike other LDA + U computations for the electronic properties of CuO that utilized the effective U-value (U_{eff}) calculated for e.g., CaCuO$_2$ and La$_2$CuO$_4$, in our case, we have self-consistently computed the U_{eff} unique to CuO using the constrained DFT + U scheme of Anisimov and Gunnarsson as implemented by Madsen and Novark in WIEN2k code. With this approach, the effective Coulomb interaction (U_{eff}) on the Cu d state is calculated self-consistently. The computed value of U_{eff} is 7.14 eV. The DFT part of the computation utilized the Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA).

Aside from the use of the DFT + U formalism, the other details of our calculations are standard. We used well converged basis sets with dense Brillouin zone samplings, which is needed for the optical properties. For this purpose we used a uniform 48x48x24 grid. The LAPW sphere radii are 1.92 and 1.71 bohr for Cu and O. We utilized the experimental monoclinic crystal structure with lattice parameter, a = 4.6837 Å, b = 3.4226 Å, and c = 5.1288 Å. All calculations were performed relativistically. We carried out several sets of self-consistent calculations using different magnetic configurations. All attempts to obtain a ferromagnetic or non-magnetic solutions always led to an antiferromagnetic ground state. This is in agreement with other results that show that CuO is an antiferromagnetic insulator. Since spin-orbit coupling (SOC) is important for CuO, reported results are for DFT + U + SOC. As mentioned, we apply no scissors operators or other adjustments.

III. RESULTS AND DISCUSSION

A. Band Structure

We begin with the calculated band structures in relation to experimental data. Our calculated band structures for CuO are given in Fig. 1. The band structures are qualitatively similar to those reported previously, but there are quantitative differences resulting from the use of the DFT + U functional, and these are important.

First of all, we note the values of the band gap. We find band gap $E_g = 1.25$ eV (1.251 eV). The calculated band gap is in accord with experimentally reported ambient temperature gap value in the range 1.0 to 1.9 eV.

We did calculations as a function of the screen Coulomb values around the self-consistently determined value of 7.14 eV (U = 5.6,7.8 eV). According to these computations, the 0.12 eV change in the band gap is too little to cause any significant change in the band gap of CuO. We also carefully checked the dependence of the gap on various computational parameters, such as energy cut-offs, energy window size for the SOC calculation, LAPW sphere radii and Brillouin zone sampling. We find that at worst the errors related to these are less than 0.08 eV in the gap. In both cases, the position of the valence band maximum and the conduction band minimum didn’t change.

The computed gap is direct and at the Γ point. This is in agreement with recent experimental results which show that CuO is a direct gap material as against some
FIG. 2: (Color online) (a) The calculated total density of states of AFM CuO. (b) The calculated projected density of states of the $x^2-y^2$-Cu 3$d$ states. (c) The calculated projected density of states of the O 2$p$ and Cu 3$d$ states. Figure 2(b) has been plotted using the local coordinate system centered on Cu where x and y axes are directed to four neighboring oxygen. The vertical straight line is the position of the Fermi energy ($E_F$) which has been set equal to zero.

reported indirect gap values in literature. The calculated magnetic moment per Cu atom (in the units of $\mu_B$) is 0.68 $\mu_B$ in good agreement with the experimental reported value of ~ 0.7 $\mu_B$. We note that the magnetic moment per oxygen atom is significant. It is 0.18 $\mu_B$ in good agreement with experiment.

B. Comparison with Angle Resolved Photoemission Spectra

Angle resolved photoemission spectra (ARPES) experiments provide a direct measure of the electronic structure of the occupied states. There have been ARPES experiments for CuO, with which we can compare.

In Fig. 2 we show the computed density of states (DOS) (Fig 2(a)) and the partial density of states (Figs. 2(b) to 2(c)) of CuO for both the spin majority and minority channels. While the bands are derived from a strong hybridization between Cu 3$d$ and O 2$p$ states, the conduction band (up to ~3.56 eV) in the proximity of the Fermi surface are formed mainly by the Cu 3$d$ (Cu 3$d_{x^2-y^2}$) states (c.f. Fig 2(b)). This corresponds to a case where there is a hole in the Cu 3$d_{x^2-y^2}$ states, the so-called 3$d^9$ configuration (we have used the local coordinate system centered on Cu where x and y axes are directed to four neighboring oxygen). In one of the earliest ab-initio study of orbital decomposition in CuO it was noted that the minority spin (Cu 3$d_{x^2-y^2}$) states contribute strongly to the conduction band minimum and the (majority spins) Cu 3$d_{x^2-y^2}$ up.

and the O 2$p$ states constitute the bands in the valence band maximum. While the bands in the proximity of the Fermi energy ($E_F$) are predominantly Cu 3$d_{x^2-y^2}$, there is a significant contribution from the O 2$p$ states. As it is evident from Figs. 2(b) and (c), the spin polarization of the states around the Fermi energy does not arise entirely from Cu 3$d_{x^2-y^2}$ states. One can reconcile the various results that claim the non-detection of the 3$d^9$ configuration (see for e.g., Ref. 52) with those that actually see it, by noting that the 3$d^9$ configuration is very complicate and observing it both in experiments and computations require very careful handling of the orbital decomposition. The most prominent feature in the conduction band is a broad peak at 2.13, 3.02, 4.97, and 5.98 eV. There is a shallow minimum around 3.62 ± 0.33 and 5.29 eV.

The states around the valence band maximum are predominantly of the O 2$p$ states hybridizing with the Cd 3$d$ (only the Cu 3$d_{x^2-y^2}$) states in agreement with ARPES result of Warren et al. (plot key Warren et al. 1999), resonant X-ray photoemission spectroscopy (XPS) results of Shen et al. and the X-ray photoemission spectroscopy results of Ghijnsen et al. One can thus conclude that the states in the proximity of the Fermi energy are basically huge band complexes of entirely the Cu 3$d_{x^2-y^2}$ and O 2$p$ states. The most prominent structure in the valence states is a peak at ~ 3.93 eV. This peak is exclusively derived from the Cu 3$d$ states.

Figure 3 shows the comparison of our computed DOS
with experiments. We reiterate that our spectra was not shifted to coincide with experiment contrary to what is often done in such comparisons with experiments (e.g. Ref. 52). As can be seen from Fig. 3, the overall valence band and the low-laying conduction band spectra are in good agreement with experimental ones. In particular, the agreement between our computed results and experimental spectra is reasonably good, both in terms of the relative intensities of the resonances and their binding energy positions. We note that there may be more features in our computed DOS as no broadening is used. Small deviation from experiment can be attributed to the fact that the intensity of photoemission spectra (PES) depend very sensitively on the photoionization across sections of the atomic sublevels. This deviation can even be seen between different experimental results.

The features from 0 to \(\approx 8.0\) eV below \(E_F\) are predominantly due to Cu 3d and O 2p states in basic agreement with the ultraviolet photoemission spectroscopy results of Tahir and Tougaard\(^\text{27}\). We calculate the valence band width to be \(\approx 8.41\) eV and the position of the maximum of the valence band is located at \(\approx 3.83\) eV in basic agreement with experimental ones with reported band width of 7.8 – 8.5 eV and the position of the valence band maximum located at 3 – 4 eV\(^\text{1,14,15,27}\) As noted earlier, no broadening is used in our calculations as such, our data show more features. Taking a closer look at the valence bands in the proximity of the Fermi energy, we find that these states are highly localized. We predict peaks at \(\approx 0.66\) eV and 1.10 eV. This feature is reminiscent of the so-called \(^1\text{A}_{1g}\) singlet\(^\text{2,11,14,15,27}\). This singlet is formed due to the hybridization of Cu 3d (mainly the Cu 3d_{x^2−y^2}) and O 2p states.\(^\text{25}\) It is the the so-called d\(^3\)L\(^1\) (where L is the ligand oxygen hole) final state with one hole in the 3d_{x^2−y^2} orbital and the other in an O 2p orbital\(^\text{2,11}\). We predict antiresonance dip around 1.23 ± 0.12 eV in basic agreement with experiment\(^\text{11}\) and a peak at 2.44 ± 0.21. There are cluster of shoulders at 3.09 ± 0.22 and 5.2 ± 0.32 eV. The ultraviolet photoemission data of Ghijsen et al.\(^\text{14}\) reported features at 1.23 ±0.11, 3.10 ±0.11, and 5.50 ±0.40 eV.

The low energy conduction band spectra show remarkable agreement with the inverse photoemission (Bremsstrahlung isochromat spectroscopy) spectra experiment of Ghijsen et al.\(^\text{14}\). Our computation predicted peaks at 2.11, 2.98 ± 0.20, and 4.97 eV.

C. Optical Properties and Comparison with Experiment

Optical spectroscopy, while less direct than ARPES, provides detailed information about the electronic structure and has the advantage of being a true bulk probe.

The optical properties of CuO in both film and bulk have been studied using several experimental methods.\(^\text{22,29,56,59}\) Most of the studies in the visible and ultraviolet have been near-normal incidence reflectivity measurements.\(^\text{29,56,58}\) These methods have certain potential sources of errors. In general, they involve multiple measurements to obtain the dielectric constants and/or Kramers-Kronig (KK) analysis, which can suffer from uncertainty in the absolute amplitude. This is associated with extrapolations necessary for the KK transformation of experimental reflectivity spectra.

Spectroscopic ellipsometry (SE) is one of the parallel measurement techniques that avoids these problems in measuring the optical constants of solids.\(^\text{60}\) The big advantage of the SE technique, and other parallel measurement techniques, is that both the real and imaginary part of the complex dielectric function of a material may be obtained directly as a function of wavelength without requiring multiple measurements or KK analysis. One of the earliest SE measurements for CuO were those of Ito and co-workers\(^\text{61}\) in the 1.2–5.0 eV photon-energy range at room temperature and that of Nomurovannaya and co-workers\(^\text{62}\).

As previously noted, we calculated optical properties based on our DFT + U electronic structure, with no adjustment. This was done using the optical properties package of the WIEN2k code. While it is conventional to plot calculated optical data with a broadening added to mimic experimental data, we instead show results with no added broadening in order to show more clearly the features in the calculated spectra. Our calculated dispersive part of the dielectric function, \(\varepsilon_1(\omega)\) and the absorptive part, \(\varepsilon_2(\omega)\) are shown in Fig. 4 in comparison with the XPS and reflection electron energy-loss spectroscopy results of Tahir and Tougaard\(^\text{27}\). As can be seen, our computed spectra for \(\varepsilon_1(\omega)\) (c.f. Fig. \(\text{4(a)}\)) and \(\varepsilon_2(\omega)\) (c.f. Fig. \(\text{4(b)}\)), are in good agreement with experiment.

There is no yet rigorous ab-initio optical property
study of CuO especially, taking into account the strong electron-electron correlations; as such, this study serves as a baseline for comparing with future experiment and theory. We emphasize that we have not employed any shift or scissors operator but have directly calculated the optical spectra from the DFT + U band structure.

Figure 4(a) shows our calculated dispersive part of the dielectric function, $\varepsilon_1(\omega)$ in comparison with the data of Tahir and Tougaard. The main experimental features in CuO are reproduced in our results. The main feature is a shoulder at 1.82 ± 0.2 eV, followed by a steep rise. We predict cluster of small shoulders at 3.05 ± 0.42 eV. Our data show a dip at ~ 3.82 eV. Experiment show a similar dip at ~ 3.68 eV. The SE data of Takayuki et al. show features at ~ 1.6, 2.0, 2.6, and 3.4 eV. We predict a shoulder at ~ 3.62 ± 0.21 eV followed by a steep decrease slowly towards almost zero at higher energies. Our computed $\varepsilon(\omega) = \Re(\varepsilon(0))$ is 6.12. The infrared spectroscopy data of Kuz'menko et al. reported $\varepsilon(\omega)$ of 5.9 – 7.8 (average value is 6.60), the SE data of Takayuki et al. reported a value of 6.45, and the polarized reflectance of a single crystal of CuO study of Homes et al. reported a value of 6.2 – 6.3. The maximum amplitude of $\varepsilon_1(\omega)$ is 11.79 ± 0.15 at 2.52 ± 0.13 eV.

Figure 4(b) shows our calculated absorptive part of the dielectric function, $\varepsilon_2(\omega)$ in comparison with the data of Tahir and Tougaard. We found a very small kink around 1.51 eV and then, shoulders around 2.40 and 2.61 eV, followed by other sets of close dips around 2.30, 2.53, and 2.82 eV; after which, the spectra increased with a steep rise in energy. The maximum of $\varepsilon_2(\omega)$ is ~ 8.96 at energy of 3.57 eV. We also find shoulders at 3.86, 4.45, and 5.41 eV; and cluster of dips at 4.24, and 4.85 ± 0.32 eV. From Fig. 4(b) both the $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ can be seen to be generally anisotropic in agreement with the SE results of Tahir and Tougaard.

Thus there is a very close correspondence between our first principles results, which represent standard band structure descriptions, and both optical data from SE and ARPES measurements.

IV. CONCLUSION

We have performed self-consistent DFT + U to study the electronic and optical properties of monoclinic CuO. Our computations show that there is significant Cu-d and O-p hybridization of the states in the proximity of the Fermi energy. Our calculated electronic structure and optical spectra are in good agreement with experiments. We obtain a band gap of 1.25 eV and local moment per Cu atom is 0.68 $\mu_B$ with significant magnetic moment of O ~ 0.18 $\mu_B$. The comparison of our calculated electronic structure with PES show generally good agreement with the key binding energies correctly obtained in our computation. So is our computed optical spectra.

Acknowledgments

Work at LSU is funded in part by the the National Science Foundation award No. EPS-1003897. V. I. Anisimov acknowledges the supports of the following. The Russian Foundation for Basic Research (Projects No. 13-02-00050 and No. 12-02-91371-CTa), the fund of the President of the Russian Federation for the support of scientific schools NSH-6172.2012.2, the Program of the Russian Academy of Science Presidium “Quantum microphysics of condensed matter” 12-P-2-1017, and the grant of the Ministry of education and science of Russia No. 14.A18.21.0076. High performance computational resources were provided by Louisiana Optical Network Initiative (LONI). C. E. Ekuma wishes to thank the Government of Ebonyi State, Nigeria.

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