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The article by Thorne Lay and Hiroo Kanamori is an interesting one. It discusses the energy released by the 1994 Northridge earthquake. The authors estimate that the earthquake released about 10¹⁵ J of energy. This is a large amount of energy, but it is only a fraction of the energy released by a 100-megaton explosion. The authors also discuss the energy released by the 1964 Chilean earthquake. They estimate that this earthquake released about 10¹⁶ J of energy. This is a much larger amount of energy than the Northridge earthquake. The authors conclude that the energy released by earthquakes is much smaller than the energy released by nuclear weapons.

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By the act of hitting a ball with a bat, one calculates the force energy to deliver the ball to its new location, but one must also take into account that the ball extended its energy release to that which became struck by the ball as its momentum ceased and passed energy to the struck item. Therefore the parameters of the damage extend into the future when the received energy to that pushed upon later becomes released in a new event. Perhaps calculations of one added that in while another's calculations did not. E.M.C.
Written by Edgar McCarroll, 14 July 2012 19:59

Understanding conductivity anomalies in Cu^I-based delafossite transparent conducting oxides: Theoretical insights

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The Cu^I-based delafossite structure, Cu^IM^{III}O₂, can accommodate a wide range of rare earth and transition metal cations on the M^{III} site. Substitutional doping of divalent ions for these trivalent metals is known to produce higher *p*-type conductivity than that occurring in the undoped materials. However, an explanation of the conductivity anomalies observed in these *p*-type materials, as the trivalent metal is varied, is still lacking. In this article, we examine the electronic structure of Cu^IM^{III}O₂ (M^{III}=Al, Cr, Sc, Y) using density functional theory corrected for on-site Coulomb interactions in strongly correlated systems (GGA+*U*) and discuss the unusual experimental trends. The importance of covalent interactions between the M^{III} cation and oxygen for improving conductivity in the delafossite structure is highlighted, with the covalency trends found to perfectly match the conductivity trends. We also show that calculating the natural band offsets and the effective masses of the valence band maxima is not an ideal method to classify the conduction properties of these ternary materials. © 2010 American Institute of Physics.
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I. INTRODUCTION

The development of “transparent electronics” is a much sought after goal for materials scientists.¹ Key materials in this quest are transparent conducting oxides (TCOs), which combine both electrical conductivity and optical transparency in a single material, usually possessing optical band gaps greater than 3 eV and carrier concentrations of at least 10²⁰ cm⁻³.² The ultimate aim is the fabrication of functional *p*-*n* junctions using these TCOs, which would open up pathways to a myriad of possible transparent electronic devices.³

n-type TCOs [In₂O₃,⁴ ZnO,⁵ and SnO₂ (Ref. 6)] are currently utilized in a number of commercial applications.⁷ Previous efforts to produce *p*-type TCOs had centered on doping the usually *n*-type TCOs to make them *p*-type, particularly ZnO.^{8,9} The top of the valence band of most wide band gap binary oxides usually is dominated by O 2*p* states, which when doped *p*-type, results in deep lying, *localized* O 2*p* holes (polarons), which are coupled to strong lattice distortions.¹⁰ These oxygen holes severely limit any electronic conduction.^{10,11}

p-type TCOs have only been a reality since 1997 when Hosono and co-workers¹² first reported the optical and electrical properties of copper aluminate (CuAlO₂), which crystallizes in the delafossite structure (Cu^IM^{III}O₂). This sparked an explosion of interest in developing *p*-type TCOs using Hosono’s “chemical modulation of the valence band” to combine the *p*-type conductivity of Cu₂O and with the larger band gaps of other binary oxides.¹³ Cu₂O is a native *p*-type semiconducting oxide with a band gap of 2.17 eV, which precludes it from TCO applications.¹⁴ Ternary Cu-based delafossite materials retain the valence band features of

Cu₂O, with the Cu states dominating the top of the valence band, while extending the band gap by alloying with the wide band gap trivalent binary oxide. Although other Cu^I-based structures have been identified that display a *p*-type conduction, e.g., SrCu₂O₂ (Refs. 15 and 16) and layered oxyhalogenides (LaCuOS,^{17,18} [Cu₂S₂][Sr₃Sc₂O₅],^{19,20} etc.), to date the *p*-type TCO with the highest conductivity is a delafossite (Mg doped CuCrO₂).²¹

In the delafossite structure, each Cu atom is linearly coordinated with two oxygen atoms, forming O–Cu–O dumbbells parallel to the *c* axis (see Fig. 1). Oxygens in these O–Cu–O units are also each coordinated to three M^{III} atoms, oriented such that M^{III}-centered octahedra form M^{III}O₂ layers, which lie parallel to the *ab* plane. Two alternative layer stackings are possible, resulting in a hexagonal (space group *P63/mmc*) or rhombohedral (space group *R3-mh*) unit cell.²²

It is well known that doping the trivalent metal site with a divalent dopant significantly improves the conductivity,¹ but the trends seen for different trivalent metal cations from Al to Cr to Sc to Y (in increasing ionic radius) remains a mystery. Nagarajan *et al.*²¹ attempted to explain the trend in increasing conductivity of CuY_{1-x}Ca_xO₂ to CuSc_{1-x}Mg_xO₂ to CuCr_{1-x}Mg_xO₂ by noting that the increasing conductivity tracks a decreasing ionic radius of the M^{III} cation, and hence a decreasing lattice parameter in the Cu ion plane. They suggested that this leads to increased Cu *d* orbital overlap and, as a result, better hole mobility. The authors also cited the need for detailed band structure calculations to examine the effect of the different M^{III} cation *d* orbitals on the valence band structure.²¹ This size dependence theory can possibly be ruled out by the observed conductivity of CuAl_{1-x}Mg_xO₂, which at 4 × 10⁻⁴ S cm⁻¹ has a much lower conductivity than that of CuCr_{1-x}Mg_xO₂ (220 S cm⁻¹), despite the ionic radius of Al being smaller than Cr.²³

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FIG. 1. The hexagonal delafossite structure. The green, red, and blue spheres are M^{III} , oxygen, and copper, respectively.

Sleight and co-workers²⁴ discussed the effect of the M^{III} ion on the mobility of holes in p -type delafossites. The authors suggested that the lower hole mobilities in p -type delafossites relative to Cu_2O may be caused by the lack of $Cu-O-Cu$ linkages as seen in Cu_2O . In the delafossite structure, there are only $Cu-O-M^{III}-O-Cu$ linkages. They suggested that the higher conductivities observed for $CuCrO_2$ and $CuFeO_2$ may be due to favorable mixing with the $3d$ states on the M^{III} cation in the $Cu-O-M^{III}-O-Cu$ linkages.²⁴

Recently, copper delafossites have been the recipient of a lot of theoretical analysis, but this has focused on band gap features, defect energetics, and the effect of doping on the band structure, and to a certain extent has neglected to look at the detailed electronic structure of these materials. Being the prototypical copper delafossite TCO, $CuAlO_2$ has received most of the attention. This has included investigating the band gap,^{25,26} intrinsic defects,²⁷ doping to form acceptor levels,²⁸ and doping for dilute magnetic semiconductor applications (both in the Cu position and the Al position²⁹). $CuAlO_2$ was investigated by Nie *et al.*,²⁶ along with $CuInO_2$ and $CuGaO_2$, using local density approximation (LDA) within the linearized augmented-plane wave (LAPW) method, reporting an indirect band gap for all three materials. An indirect band gap was also reported by Robertson and co-workers,²⁵ who investigated the hexagonal cell of $CuAlO_2$ using LDA. The layer stacking has a little effect on the minimum gap, with an indirect gap of 2.1 eV predicted for both the hexagonal and rhombohedral sequences.

A LDA study of native defects in $CuAlO_2$ was also carried out by Hamada *et al.*²⁷ which postulated that copper vacancies and oxygen interstitials are the relevant defects, and that control of the copper and oxygen partial pressures is essential for the fabrication of low-resistivity $CuAlO_2$. The effects of Cu and Al vacancies, and Be, Mg, and Ca dopants on the electronic structure of $CuAlO_2$ have also been inves-

tigated using LDA based LAPW calculations,²⁸ with the results showing that the most promising defects for improving p -type conductivity are Cu vacancies and Be doping at Al sites.

$CuScO_2$ and $CuYO_2$ have received sparse attention, with only a handful of theoretical investigations in literature.^{30–33} Gilliland *et al.*³⁰ studied the band structure of $CuScO_2$ using LDA. They reported a direct band gap at L , but did not report the band gap magnitude.³⁰ Shi and co-workers studied intrinsic³¹ and extrinsic³² defects in $CuScO_2$ and $CuYO_2$. They reported that the copper vacancies and oxygen interstitials have relatively low formation energies in these materials, and that under oxygen rich conditions, the oxygen anti-site becomes an important acceptor.³¹ Mg and Ca dopants are found to be the most prominent extrinsic defects.³² A recent study by Li and co-workers³³ investigated the band edge features of $CuM^{III}O_2$ ($M^{III}=Al, Y, Sc$) and calculated the valence band alignment [valence band maximum (VBM)] of these materials to ascertain why $CuScO_2$ shows the best conductivity of the three. They found that $CuScO_2$ has the lowest hole effective mass and the highest VBM relative to the vacuum of all three, and concluded that these factors make $CuScO_2$ the most conductive.³³

$CuCrO_2$ has only recently received some theoretical attention, with this group's study of the band structure and density of states of both the rhombohedral and hexagonal cells.^{34,35} Our calculated simulated x-ray photoemission spectroscopy (XPS) for $CuCrO_2$ is in excellent agreement with x-ray photoelectron spectroscopy results, indicating that the Cr states cause an oxygen mediated effect on the Cu d states at the top of the valence band.³⁵ Very recently, Eyert and co-workers³⁶ investigated the electronic structure of $CuCrO_2$ using generalized gradient approximation (GGA) within the augmented spherical wave method. The authors presented spin polarized partial electronic densities of states (PEDOSs) for the rhombohedral representation of the $CuCrO_2$ cell. This four atom cell cannot therefore take into account the antiferromagnetic (AF) nature of $CuCrO_2$,³⁷ and hence this study is restricted to the higher energy ferromagnetic (FM) configuration.³⁶ The PEDOS reports that Cr $3d$ t_{2g}^3 states dominate at the top of the valence band, ~ 1.5 eV above the Cu $3d$ peak,³⁶ although this is inconsistent with high resolution XPS studies, which show that Cu states dominate at the VBM.³⁵

In this work, we systematically study the effect of the M^{III} cation on the electronic structure and chemical bonding of $CuM^{III}O_2$ ($M^{III}=Al, Y, Sc, Cr$). We demonstrate the importance of the increased covalency between the M^{III} states and oxygen as we move from Al to Y to Sc to Cr. We will also discuss the experimentally seen conductivity trends in doped Cu-based TCOs using the doping limit rule, effective mass theory, and our knowledge of the detailed electronic structure of the materials.

II. CALCULATION METHODOLOGY

Structural optimizations were performed on the hexagonal $CuM^{III}O_2$ (space group $P63/mmc$) cells using density functional theory (DFT),^{38,39} as implemented in the VASP

TABLE I. Structural data and nearest-neighbor interatomic distances for the optimized $\text{CuM}^{\text{III}}\text{O}_2$ ($\text{M}^{\text{III}} = \text{Al}, \text{Cr}, \text{Sc}, \text{Y}$) structures. Percentage errors with respect to the experimental data [CuAlO_2 (Ref. 22), CuCrO_2 (Ref. 58), CuScO_2 (Ref. 59), and CuYO_2 (Ref. 60)] are given in parentheses. Volumes are given in $\text{\AA}^3$ and lattice dimensions and interatomic distances in $\text{\AA}$.

	CuAlO_2	CuCrO_2	CuScO_2	CuYO_2
Volume	81.79	92.50	104.47	125.90
a	2.885(+0.7%)	3.055(+2.9%)	3.248(+0.7%)	3.562(+1.1%)
c	11.340(+0.2%)	11.416(+0.1%)	11.429(+0.1%)	11.454(+0.1%)
Cu–O	1.866	1.844	1.832	1.821
$\text{M}^{\text{III}}\text{–O}$	1.928	2.032	2.138	2.306

(Refs. 40 and 41) code. Exchange and correlation were described using the GGA, within the Perdew–Burke–Ernzerhof⁴² formalism. The core electrons ($\text{Cu}:[\text{Ar}]$, $\text{Al}:[\text{Ne}]$, $\text{Y}:[\text{Ar}]$, $\text{Sc}:[\text{Ne}]$, $\text{Cr}:[\text{Ar}]$, and $\text{O}:[\text{He}]$) were treated within the projector augmented method.⁴³ In each case the atomic positions, lattice vectors, and cell angles were allowed to relax, while the total volume was held constant. The resulting energy volume curves were fitted to the Murnaghan equation of state to obtain the equilibrium bulk cell volume.⁴⁴ This approach avoids the problems of Pulay stress and changes in the basis set which can accompany volume changes in plane wave calculations. Convergence with respect to k -point sampling and plane wave energy cutoff was checked, and for all systems, a Monkhorst Pack k -point grid of $9 \times 9 \times 5$ and a plane wave cutoff of 500 eV were found to be sufficient. Calculations were performed using DFT corrected for on-site Coulombic interactions GGA+ U (Ref. 45) to overcome the errors associated with the DFT self-interaction. GGA typically underbinds localized orbitals such as metal d states, and the + U modification provides an approximate correction for this shortcoming.⁴⁶ The validity of the GGA+ U approach has been demonstrated in its recent use to provide improved descriptions of a wide range of localized electronic defect system including strongly correlated n -type materials^{47–51} and p -type systems.^{52,53}

The U value chosen for the Cu d was 5.2 eV, which closely reproduces features of the experimental XPS spectra for Cu_2O and has been shown to reproduce the valence band features of both CuAlO_2 (Ref. 34) and CuCrO_2 .³⁵ This U is also similar to the U values used by Raebiger *et al.* of 5 eV (which was also chosen to reproduce features of a Cu_2O XPS valence band spectra⁵⁴), and the value of 6 eV chosen by Huda *et al.* to account for the correlation in narrow $3d$ bands.⁵⁵ A U value of 4 eV for the Cr d states has been shown to reproduce the valence band features of Cr_2O_3 .⁵⁶ All the calculations of CuCrO_2 , which contains open- d shells Cr atoms, were spin polarized. Calculations were deemed to be converged when the forces on all the atoms were less than $0.001 \text{ eV \AA}^{-1}$. Structure visualization and analysis were performed using VESTA.⁵⁷

III. RESULTS

A. Structure

The optimized structural parameters of $\text{CuM}^{\text{III}}\text{O}_2$ ($\text{M}^{\text{III}} = \text{Al}, \text{Y}, \text{Sc}, \text{Cr}$) are shown in Table I. In all our delafossites,

the calculated lattice constants are slightly overestimated, but this is a known overestimation associated with GGA calculations. The calculated bond lengths for each material are in good agreement with experimentally determined measurements.^{22,58–60} The lattice parameter a increases for Al–Cr–Sc–Y, consistent with the trend in the cation M^{III} sizes. It has been suggested that the larger M^{III} cations can improve the capacity of a material for extrinsic doping on the M^{III} site, which can result in high hole concentrations,³³ and this has been used to explain the more promising p -type conductivity of doped CuScO_2 and CuYO_2 compared to that of the smallest cation CuAlO_2 . This, however, does not explain the much higher p -type conductivity of Mg doped CuCrO_2 , considering it has a smaller M^{III} cation size than both CuYO_2 and CuScO_2 . Nagarajan *et al.*²¹ suggested that a decrease in the cation M^{III} size, increases the Cu d - d overlap, resulting in greater conductivity. This would explain the trend in increasing conductivity for CuYO_2 to CuSc_2 to CuCrO_2 but cannot explain the poor conductivity observed for CuAlO_2 .

B. Electronic structure

1. CuAlO_2

The calculated band structure of CuAlO_2 is shown in Fig. 2. The conduction band minimum (CBM) is positioned at Γ and a broad, flat VBM is found along the H–K line and extends past K in the K – Γ direction. This is in good agreement with previous calculations,²⁶ but is at variance with the

FIG. 2. The electronic band structure of CuAlO_2 along the high symmetry points, plotted with reference to the top of the valence band at 0 eV. The green shaded area denotes the band gap.

FIG. 3. The electronic density of states for CuAlO_2 . (a) Total EDOS, (b) Cu PEDOS, (c) Al PEDOS, and (d) O PEDOS. The blue lines represent d states, green lines represent s states, and red lines represent p states.

study by Robertson *et al.*,²⁵ which predicted that the VBM is situated at L . In our present study, the highest occupied band at the L k -vector is 0.1 eV below the VBM. This results in an indirect band gap of 2.2 eV. Although this is an overestimation compared to the value of 1.8 eV obtained from optical-absorption experiments,⁶¹ it has been proposed that intrinsic defect levels decrease the experimental value.²⁵ A direct band gap of 3.1 eV is found at Γ , compared to 3.5 eV found by experiment.⁶¹

Figure 3 shows the calculated total and partial (ion decomposed) electronic densities of states (EDOS/PEDOS) for CuAlO_2 . Four distinct peaks are found in the valence band, consistent with a recent XPS study reported by Aston *et al.*⁶² The conduction band consists of a narrow peak (labeled V) between 2 and 4 eV and a second broader peak above 6 eV.

The Cu PEDOS is dominated by $3d$ states between -4 and -1 eV, corresponding to peaks III and IV in the EDOS. There are also Cu $3d$ states between -9 and -4 eV, indicating a degree of covalent bonding with oxygen. The Al PEDOS shows a small valence band contribution concentrated between -9 and -4 eV, which consists of a mixture of $3s$, $3p$, and $3d$ states. In the conduction band the onset of Al states does not occur until $+5$ eV. The Al contributions to the EDOS are small, as expected for an atom which is often well described by a fully ionized $+3$ oxidation state, and Al makes a minimal contribution to the states determining the electronic conduction properties. The O PEDOS displays all four peaks observed in the EDOS. Peak I is O $2p$ in nature with a minor contribution from Al $3s$ and $3p$ states. Peak II is mainly O $2p$ although Cu $3d$ states are also present. Peak III is mostly Cu $3d$ with some O $2p$ contribution. The bottom of the conduction band (peak V) and top of the valence band (peak IV) both consist of states derived from a mixture of Cu $3d$ and O $2p$.

2. CuCrO_2

The band structure (Fig. 4) for CuCrO_2 exhibits an indirect band gap of 2.04 eV, with a direct gap measuring 2.55

FIG. 4. The electronic band structure of CuCrO_2 along the high symmetry points, plotted with reference to the top of the valence band at 0 eV. The green shaded area denotes the band gap.

eV found near M along M - Γ . For CuCrO_2 there is an experimentally demonstrated redshift in the experimental optical-absorption relative to CuAlO_2 . The CBM is centered between L and A and the VBM is situated at M . This was also found to be the case for 50% Cr doped CuAlO_2 .³⁴ The presence of two Cr sites introduces the possibility of magnetic ordering within the periodicity of the simulated unit cell. Due to the t_{2g}^3 configuration, AF interactions are stabilized, while FM interactions result in no net energy gain. The calculated energy difference between the AF and FM configurations is small at 20 meV/f.u., which is consistent with the low Curie temperature that has been noted in experiment.⁶³

The EDOS of CuCrO_2 is shown in Fig. 5. The valence band features are very similar to those reported by Arnold *et al.* in a recent XPS study.³⁵ These features are different from those of CuAlO_2 , with a significant shoulder appearing on the higher energy side of the main peak (peak III) at ~ -1.5 eV. In the Cu PEDOS, the Cu peak shape is also affected: the shoulder to the left of the maximum just below -2 eV is less pronounced, and a second shoulder now ap-

FIG. 5. The electronic density of states for CuCrO_2 . (a) Total EDOS, (b) Cu PEDOS, (c) Cr PEDOS, and (d) O PEDOS. The blue lines represent d states, green lines represent s states, and red lines represent p states.

FIG. 6. The electronic band structure of CuScO_2 along the high symmetry points, plotted with reference to the top of the valence band at 0 eV. The green shaded area denotes the band gap.

pears to the high energy side of the main peak. The Cr states appear along the entirety of the valence band, with a significant peak at ~ -2.5 eV, and with the Cr contribution to peak IV increasing the density of states at the top of the valence band relative to that of CuAlO_2 . The O 2p states dominate the lower valence band, with peaks I and II being made up mainly of O 2p states, but with significant contributions from Cu *d* and Cr *d* states. The bottom of the conduction band is predominantly Cr in nature, with the contribution from O 2p states now extending up to ~ 5 eV due to increased interaction with the Cr 3d. This increased Cr–O interaction compared to Al–O in CuAlO_2 is likely to be responsible for the change in the *k*-vector of the CBM away from Γ .

3. CuScO_2

The band structure of CuScO_2 is shown in Fig. 6. The VBM is situated at H, with the CBM lying at Γ . Previous studies by Shi *et al.*³³ and Gilliland *et al.*³⁰ have reported a direct band gap for CuScO_2 , but these studies were carried out using the smaller rhombohedral cell, although it has been shown that CuScO_2 forms preferentially in the hexagonal structure.⁵⁵ The indirect band gap measures 2.88 eV with the smallest direct band gap measuring 2.98 eV at the *M* point. Experiment reports the band gap of CuScO_2 to be 3.3 eV.⁶⁴

Figure 7 shows the calculated total and partial EDOS for CuScO_2 . The valence band consists of six distinct peaks (labeled I–VI) with the conduction band consisting of two large peaks (VII and VIII). The Cu PEDOS is dominated by 3d states between -4 and 0 eV, but also features some 3d states between -6 and -4 eV, indicating some covalency with the oxygen states. The Sc PEDOS shows a very minor valence band contribution. However, the conduction band is dominated by Sc *d* states, which make up the vast majority of peaks VII and VIII. As is the case for Al in CuAlO_2 , the Sc states in CuScO_2 are not expected to have a significant contribution to the states determining the electronic conduction properties. The O PEDOS shows that O plays a dominant role in three of the peaks at the lower end of the valence band spectrum, and a significant role in peak V. Peaks I and II are primarily O 2p in nature with some interaction with Cu 3d, peak III is of mainly O 2p character with some signifi-

FIG. 7. The electronic density of states for CuScO_2 . (a) Total EDOS, (b) Cu PEDOS, (c) Sc PEDOS, and (d) O PEDOS. The blue lines represent *d* states, green lines represent *s* states, and red lines represent *p* states.

cant Cu 3d hybridization. Peaks IV–VI are dominated by Cu 3d states with some significantly O 2p contribution to peak V. The conduction band make-up (peaks VII and VIII) is dominated by Sc *d* states, with some slight mixing of O 2p states, indicating some $\text{M}^{\text{III}}\text{–O}$ interaction, which was not present in CuAlO_2 .

4. CuYO_2

The calculated band structure for CuYO_2 is shown in Fig. 8. The VBM is situated at H, similar to the band structure for CuScO_2 . The CBM is located at Γ , giving an indirect band gap of 2.93 eV, which is consistent with the work of Shi *et al.*,³³ which also reported an indirect band gap for CuYO_2 . They reported a calculated indirect band gap of 2.63 eV, which is an underestimation compared to our calculated value. This is to be expected, as we have used GGA+*U*, which although not a method to be used for absolute band gap correction, does often result in better descriptions of

FIG. 8. The electronic band structure of CuYO_2 along the high symmetry points, plotted with reference to the top of the valence band at 0 eV. The green shaded area denotes the band gap.

FIG. 9. The electronic density of states for CuYO_2 . (a) Total EDOS, (b) Cu PEDOS, (c) Y PEDOS, and (d) O PEDOS. The blue lines represent d states, green lines represent s states, and red lines represent p states.

band gaps than GGA.⁴⁶ The smallest direct gap is located at Γ , and measures 3.15 eV, compared to the experimentally reported band gap of ~ 3.5 eV.⁶⁵

The calculated total and partial EDOS for CuYO_2 is displayed in Fig. 9. The valence band shows five distinctive peaks (labeled I–V), with two peaks present in the conduction band (VI and VII). Similar to CuScO_2 , the Cu PEDOS is dominated by Cu d states between -3 eV and the VBM, but there are some significant Cu d states between -6 and -3 eV. The Y PEDOS valence band features are also similar to that of CuScO_2 , with the Y d and p states only having a small contribution. However, the Y d states dominate the conduction band of the Y PEDOS, corresponding to peaks VI and VII on the total EDOS. The oxygen PEDOS shows us that peaks I–III in the total EDOS are primarily of O $2p$ character, with some Cu d mixing and some very minor contributions from Y states. Peaks IV and V are made up of Cu d states, with some significant mixing with O $2p$ states. Some small O $2p$ contributions are noted in the conduction band, indicating a degree of interaction between the yttrium and oxygen, similar to CuScO_2 .

C. Bader analysis

It is clear from the analysis of the valence band features of the four delafossites that the greatest interaction between M^{III} states and the valence band is seen for CuCrO_2 . While Sc states in CuScO_2 and Y states in CuYO_2 both appear to interact with the O $2p$ states in the conduction band (more than the O $2p$ states interact with Al states in the conduction band of CuAlO_2), they have no major interactions with the states that will determine the p -type conduction properties of these materials, at the top of the valence band. It is instructive at this point to quantify how the distribution of charges changes as we vary the M^{III} cation from Al–Cr–Sc–Y using Bader⁶⁶ partial charge analysis.

The calculated Bader charges are listed in Table II. Al

TABLE II. Bader partial electron charges for CuAlO_2 , CuCrO_2 , CuScO_2 , and CuYO_2 .

	CuAlO_2	CuCrO_2	CuScO_2	CuYO_2
Cu	+0.52	+0.52	+0.52	+0.51
M^{III}	+2.48	+1.68	+2.03	+2.18
O	−1.50	−1.10	−1.27	−1.34

has a charge of $+2.48e$ in CuAlO_2 , in comparison to a formally ionic state of $+3e$. This result highlights the ionicity of Al in this system. The charges for Cu ($+0.50e$) and O ($-1.49e$) are less than would be expected from the purely ionic model, but are consistent with the calculated densities of states, which show significant covalent mixing between the Cu and O in the valence band states.

Analysis of CuCrO_2 gives charges of $+0.52e$ for Cu, $+1.68e$ for Cr, and $-1.10e$ for O, which indicate covalent mixing between all three species. All three ions are significantly less ionic than their formal oxidation states suggest, and indeed O is considerably less ionic than it is in CuAlO_2 . This indicates partial charge transfer from O to Cr and that the amount of charge transfer from O to Cu is not affected. This supports the interpretation of the PEDOS that Cr contributes significantly to the top of the valence band and bottom of the conduction band.

For CuScO_2 , charges of $+0.52e$ for Cu, $+2.03e$ for Sc, and $-1.27e$ for O are found, again indicating valence charge being distributed between the three species. The fact that the O and Sc results are slightly more ionic than O and Cr in CuCrO_2 indicates that there are definitely less covalent interactions in CuScO_2 than CuCrO_2 , as is evidenced by the PEDOS, where Sc states do not play a major role in the valence band make-up, but do interact with O in the conduction band.

The results for CuYO_2 are similar to CuScO_2 , with charges of $+0.51e$ for Cu, $+2.18e$ for Y, and $-1.34e$ for O being found. This again indicates that the covalent interactions are smaller in this system between the O and Y states, with both being more ionic than the charges on Sc and O in CuScO_2 . This again is similar to the analysis of the EDOS/PEDOS, which shows some covalency between Y d states and O $2p$ in the conduction band, but virtually none in the valence band, leading to a more ionic description of Y and O states in CuYO_2 when compared to CuScO_2 and CuCrO_2 .

D. Effective hole masses of the VBM

A common method used to determine the conductive ability of a material is to calculate the effective mass of the band edges. In the case of p -type TCOs, the hole effective mass at the VBM should indicate the p -type conduction properties of a material. The effective mass (m^*) is calculated using

$$\frac{1}{m^*(E)} = \frac{1}{\hbar^2 k} \frac{dE}{dk}, \quad (1)$$

where $E(k)$ is the band edge energy as a function of wave vector k , obtained directly from the GGA+ U calculation.⁶⁷

TABLE III. Table showing the effective masses (in units of free electron mass, m_0) for CuAlO₂, CuCrO₂, CuScO₂, and CuYO₂, calculated using GGA+*U* and GGA+*U* with spin-orbit coupling. m_{100} , m_{010} , and m_{001} are the effective masses in the [100], [010], and [001] directions, respectively.

	GGA+ <i>U</i>			GGA+ <i>U</i> +SO		
	m_{100}	m_{010}	m_{001}	m_{100}	m_{010}	m_{001}
CuAlO ₂	2.60	2.60	58.43	2.60	2.60	38.95
CuCrO ₂	2.96	2.96	7.21	4.53	4.53	6.07
CuScO ₂	4.00	4.00	8.22	4.00	4.00	8.22
CuYO ₂	4.21	4.21	7.16	3.72	3.72	7.64

In this way, the diagonal elements of the effective mass tensor can be calculated for a certain *k*-point.

The premise of effective mass theory relies on parabolic bands at the band edges. Although there is some slight curvature at the VBM for the four delafossites examined in this study, the high densities of states around the VB maxima means that the bands are far from parabolic, and thus are not expected to be well described under a typical semiconductor effective mass approximation.⁶⁷ Despite this, we report the effective masses of the VBM for each material as a rough guide to the conduction properties of each material. We also report the effective masses calculated using spin-orbit coupling, as this has been shown previously to split the doublet VBM of other copper based *p*-type TCOs and to have a big effect on the corresponding effective masses.⁶⁸

Table III shows the calculated effective hole masses for the four delafossites involved in this study. The effective masses in the [100] and [010] directions are isotropic, which is to be expected for the hexagonal representation of the delafossite structure. A recent study by Shi *et al.*³³ using the rhombohedral cell found the effective masses to be anisotropic in three directions. They noted the smallest effective masses were in the [001] direction, which they stated was due to the O–Cu–O chain along that direction offering a channel for hole transfer.³³ In our results, we find that effective masses are largest in the [001] direction, with the effective mass of CuAlO₂ in the [001] being a rather large 58.43 m_0 . This indicates a virtually flat band, which agrees with analysis of the band structure of CuAlO₂ at the valence band edge. Surprisingly, the delafossite with the smallest effective mass in the [001] direction is CuYO₂. This is at variance with the results of Shi *et al.*, who found that the effective masses of CuScO₂ were lower than that of CuYO₂ and CuAlO₂. This, however, is based on the average of the effective masses in the three directions.³³ Indeed, the effective mass of CuYO₂ in the [001] direction is found to be lower than that for CuScO₂ and CuAlO₂, meaning CuYO₂ should find it easiest to conduct along the O–Cu–O channels.³³ It is clear from the results that we have obtained that applying effective mass theory to this type of material is not accurate. These systems do not have parabolic bands and have been shown experimentally in the cases of CuAlO₂,⁶⁹ CuScO₂,⁷⁰ and CuYO₂ (Ref. 70) to conduct via polaronic hopping mechanisms, which are not well described by effective mass theory. As the holes are expected to hop from Cu to Cu,⁷¹ it is not surprising that the effective masses in the [100] and [010] directions are lowest, indicating that conduction in

delafossites will most likely take place in the *ab* Cu–Cu plane, and not in the [001] plane through the M^{III}O₂ layers. Thus, we tentatively suggest that all we can really take from these calculations is that, on the average, the effective mass of holes at the VBM of CuYO₂, CuScO₂, and CuCrO₂ are smaller than that of CuAlO₂ and that, on the average, the effective masses for CuCrO₂ are lowest.

E. Valence band alignments

It has become popular among the theoretical physics community to calculate the “natural” valence band alignments of different materials and thus rank them according to the doping limit rule.^{72,73} This type of analysis has previously been carried out for Cu(Al/In/Ga)O₂ (Ref. 26) and for Cu(Al/Sc/Y)O₂.³³ Although these are separate studies from different authors, the authors of the latter study used the approximate transitivity of the of band offsets⁷⁴ to compare the alignments in both studies. They concluded that CuScO₂ has the highest VBM of the five delafossites, and therefore is easier to dope *p*-type, according to the doping limit rule.³³

We calculate the valence band alignments according to the method developed by Wei and Zunger,^{74,75} which does not take into account the deformation potentials of the core states.^{76,77} Heterostructures of 1 × 1 × 8 were constructed in the [001] direction, resulting in 48 and 64 atom superlattices made up of a 50-50 mix of CuAO₂/CuBO₂. The lattice constants of CuAO₂ and CuBO₂ are averaged and used as the lattice constant of the superlattice. All the atoms in the heterostructure are relaxed until the forces on each atom are less than 0.01 eV Å⁻¹.

The valence band offsets are thus given by

$$\Delta E_V^{\text{CuA/BO}_2} = \Delta E_{\text{VBM-CL}}^{\text{CuAO}_2} - \Delta E_{\text{VBM-CL}}^{\text{CuBO}_2} + \Delta E_{\text{CL}_A\text{-CL}_B}^{\text{CuA/BO}_2}, \quad (2)$$

where $\Delta E_{\text{VBM-CL}}^{\text{CuAO}_2} = E_{\text{VBM}}^{\text{CuAO}_2} - E_{\text{CL}}^{\text{CuAO}_2}$ and $\Delta E_{\text{VBM-CL}}^{\text{CuBO}_2} = E_{\text{VBM}}^{\text{CuBO}_2} - E_{\text{CL}}^{\text{CuBO}_2}$. These are the core level (CL) to VBM separations for pure CuAO₂ and CuBO₂ at their equilibrium lattice constants. $\Delta E_{\text{CL}_A\text{-CL}_B}^{\text{CuA/BO}_2} = E_{\text{CL}_A}^{\text{CuA/BO}_2} - E_{\text{CL}_B}^{\text{CuA/BO}_2}$ is the difference in the CL binding between the CLs in the constituent halves of the heterostructure.

As different studies have used different representative CLs, we have calculated the alignments in three ways: using the O 1s levels, using the Cu 1s levels, using the M^{III} 1s levels, and using the average energy of the 1s levels of Cu, M^{III}, and O as the energy of the CL. The calculated alignment results for the three different methodologies are shown in Table IV. It is clear for the calculated alignments that the

TABLE IV. The GGA+*U* natural band alignments of $\text{CuM}^{\text{III}}\text{O}_2$ ($\text{M}^{\text{III}}=\text{Al}, \text{Sc}, \text{Cr}, \text{Y}$) calculated using the O 1s states; the Cu 1s states; the M^{III} 1s; and the average of the Cu 1s, O 1s, and M^{III} 1s states as the core levels (denoted $\langle 1s \rangle$). CuScO_2 is taken as the reference level in all four alignments.

	O 1s	Cu 1s	M^{III} 1s	$\langle 1s \rangle$
CuAlO_2	-0.01	+0.29	-1.52	-0.41
CuCrO_2	+0.07	+0.22	-0.63	-0.11
CuScO_2	0.00	0.00	0.00	0.00
CuYO_2	-0.016	-0.19	+1.05	+0.23

choice of CL has a big influence on the resultant alignment, with all four methods showing vastly different trends. Considering that the original study on $\text{Cu}(\text{Al}/\text{In}/\text{Ga})\text{O}_2$ used CLs which they did not specify²⁶ and the study of $\text{Cu}(\text{Al}/\text{Sc}/\text{Y})\text{O}_2$ used the average of the 1s levels of Cu, M^{III} , and O,³³ we would have to question the accuracy of applying the approximate transitivity of band offsets between alignment studies using different CLs when you take into account the difference the choice of CLs has on the alignment. Using the M^{III} 1s states, on their own, or as part of an average, definitely distorts the alignment hugely compared to the alignments from the Cu 1s states or the O 1s states. None of the alignment methodologies used are consistent with the observed experimental conductivity trends, which would suggest that the trend should be Cr–Sc–Y–Al in the order of highest VBM to lowest VBM. In fact, the difference in trends between the different CL choices must call into question the use of this method to calculate alignments for copper based ternary oxides. It should also be noted that the errors associated with this method can be rectified by calculating the absolute deformation potential of these materials, which should in principle account for variations in the core levels, but is too expensive and time consuming to calculate for noncubic systems.⁷⁸

IV. DISCUSSION

Since the first report of *p*-type transparent conductivity in the $\text{CuM}^{\text{III}}\text{O}_2$ structure in 1997, interest in these materials has been intense. Despite the repeated findings of poor conductivity compared to their *n*-type TCO counterparts, $\text{CuM}^{\text{III}}\text{O}_2$ TCOs retain popularity as a viable platform for future high performance *p*-type TCO applications.^{79,80} In addition, delafossite structured materials have started to receive attention as potential electrodes in photoelectrochemical (PEC) water splitting,^{65,81–88} in spite of the fact that in many cases their band gaps are far in excess of the required range for PEC applications (1.7–2.2 eV).⁸⁹

It is clear from our results that due to the polaronic nature of these Cu^{I} oxides,^{69,70,90} effective mass theory is not an ideal way to rank the conductivity properties of delafossite materials. Further to this, calculating the natural valence band offsets for these ternary copper materials using the Wei and Zunger approach^{74,75} does not yield any worthwhile information, and we have demonstrated that the trends are extremely sensitive to the choice of CL used in the analysis. Although these methods have been used quite successfully

for simple binary materials,^{72,73} accurate band offsets for ternary delafossites do not seem possible using this method.

As delafossites and Cu^{I} oxides, in general, are known to be polaronic,^{69–71,90–100} it is expected that the Cu–Cu distances should play a part in any conductivity, as holes are expected to hop from Cu to Cu.⁷¹ The Cu–Cu distance (equal to the *a/b* lattice constant) is determined by the size of the M^{III} ion, which suggests that the conductivity will increase as the size of the M^{III} ion decreases. In fact, this seems to be true for CuBO_2 , which has the smallest Cu–Cu distance of all delafossites, and is reported to have the highest nondoped conductivity.⁷⁹ This would also explain why undoped CuAlO_2 has been reported to have a higher conductivity than both nondoped CuScO_2 and CuYO_2 .²³

Unfortunately, conduction in these systems is more complex than simply stating that conductivity is inversely proportional to the M^{III} radii size. The number of hole carriers (introduced by intrinsic or extrinsic defects) in the system is also very important, with size of the M^{III} again playing a leading role. The size of the M^{III} plays another role in determining the nondoped conductivity of these materials, as the larger the M^{III} ion, the more oxygen interstitials the material can contain.^{24,101} This conceivably explains why CuYO_2 (Ref. 24) is reported to have a higher nondoped conductivity than CuScO_2 .¹⁰² It cannot, however, explain why CuCrO_2 has a higher undoped conductivity even than CuAlO_2 .²³

Similarly, as the size of the M^{III} ion increases, so too does the ability to dope the material.³³ By this rationale, extrinsic doping of CuAlO_2 to increase carrier concentrations and lower the Fermi level could be substantially more difficult than doping CuYO_2 , for instance. It is known that there is a very limited range for Mg^{II} substitution in CuCrO_2 , with $x=0.05$ being the limit for $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$.³⁶ Despite this, the conductivity of $\text{CuCrO}_2:\text{Mg}$ is much higher than that of $\text{CuScO}_2:\text{Mg}$ and CuYO_2Ca , which should be able to contain a much higher dopant concentration. Electronic structure of the M^{III} ion must therefore also play a key role in conductivity.

If we analyze the Bader charges for the four delafossites studied, we can see that the trend of M^{III} ion covalency with oxygen follows Cr–Sc–Y–Al, with Cr having the largest covalent interaction. This follows exactly the experimentally known conductivity trend for the doped delafossites. This is not unexpected, as elementary chemical intuition tells us that a more delocalized, covalent valence band would be optimal for hole mobility enhancement.

It is clear from these results that conductivity in these systems is a synergy between both size and electronic structure of the M^{III} ions. The important requirements for good conductivity would appear to be (i) the M^{III} ion not being overly large, and thus not limiting the hole hopping, leading to good nondoped conductivity; (ii) the M^{III} ion having a favorable electronic structure, which can enhance the mobility of holes; and (iii) the M^{III} ion not being too small and limiting the dopability of the material and hence allowing a high charge carrier concentration. Finding a compromise between these three factors is the key and might plausibly explain why CuCrO_2 is currently the leading material, possess-

ing a favorable electronic structure, and an M^{III} ion big enough to allow doping and small enough not to limit hopping.

V. CONCLUSION

The electronic structure and geometry of $CuM^{III}O_2$ ($M^{III}=Al, Y, Sc, Cr$) have been calculated using GGA+ U . The calculated band structures and atom decomposed densities of states have been reported. The influence of the d states of Y, Sc, and Cr on the density of states is investigated, with the Cr d states of $CuCrO_2$ having the greatest influence on the valence band makeup of the delafossites. Bader analysis indicates that the covalent interactions between the trivalent metal and oxygen follow the trend $Al-Y-Sc-Cr$ with Cr having the greatest covalent interaction with oxygen. This trend follows the experimental trend of conductivity in doped delafossites. Thus, we conclude that favorable cation size and favorable mixing between the d states of the M^{III} ion and the O $2p$ states determines the mobility and conduction in these delafossite type materials.

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