Understanding conductivity anomalies in CuI-based delafossite transparent conducting oxides: Theoretical insights

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(Received 20 November 2009; accepted 15 December 2009; published online 12 January 2010)

The CuI-based delafossite structure, CuIMIIIO2, can accommodate a wide range of rare earth and transition metal cations on the MIII 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 CuIMIIIO2 (MIII=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 MIII 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.

[i]doi:10.1063/1.3290815

I. INTRODUCTION

The development of “transparent electronics” is a much sought after goal for materials scientists. 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. The ultimate aim is the fabrication of functional n-type, particularly CuI-based transparent conducting oxides (TCOs), which would open up pathways to a myriad of possible transparent electronic devices. n-Type TCOs [In2O3,7 ZnO,8 and SnO2 (Ref. 6)] are currently utilized in a number of commercial applications. Previous efforts to produce n-type TCOs had centered on doping the usually n-type TCOs to make them p-type, particularly ZnO.9 The top of the valence band of most wide band gap binary oxides usually is dominated by O 2p states, which when doped p-type, results in deep lying, localized O 2p holes (polarons), which are coupled to strong lattice distortions. These oxygen holes severely limit any electronic conduction. 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 (CuAl2O4), which crystallizes in the delafossite structure (CuIMIIIO2). 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 CuI and with the larger band gaps of other binary oxides. CuI is a native p-type semiconductor oxide with a band gap of 2.17 eV, which precludes it from TCO applications. Ternary Cu-based delafossite materials retain the valence band features of CuI 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-based structures have been identified that display a p-type conduction, e.g., SrCuO2 (Refs. 15 and 16) and layered oxycarbonate s (LaCuOS,15,16 [Cu5S2][Sr3Sc2O13],18,20 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–O units are also each coordinated to three MIII atoms, oriented such that MIII-centered octahedra form MIIIO2 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 R3-1m) unit cell.22

It is well known that doping the trivalent metal site with a divalent dopant significantly improves the conductivity, 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 CuY1−xO2 to CuSc1−xMg2xO2 by noting that the increasing conductivity tracks a decreasing ionic radius of the MIII cation, and hence a decreasing lattice parameter in the Cu-I 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 MIII cation d orbitals on the valence band structure.21 This size dependence theory can possibly be ruled out by the observed conductivity of CuAl1−xMg2xO2, which at 4 × 10−4 S cm−1 has a much lower conductivity than that of CuCr1−xMg2xO2 (220 S cm−1), despite the ionic radius of Al being smaller than Cr.23

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Slieght and co-workers\cite{24} discussed the effect of the $\text{M}^{\text{III}}$ ion on the mobility of holes in $p$-type delafossites. The authors suggested that the lower hole mobilities in $p$-type delafossites relative to $\text{Cu}_2\text{O}$ may be caused by the lack of $\text{Cu}–\text{O}–\text{Cu}$ linkages seen in $\text{Cu}_2\text{O}$. In the delafossite structure, there are only $\text{Cu}–\text{O}–\text{M}^{\text{III}}–\text{O}–\text{Cu}$ linkages. They suggested that the higher conductivities observed for $\text{CuCrO}_2$ and $\text{CuFeO}_2$ may be due to favorable mixing with the 3$d$ states on the $\text{M}^{\text{III}}$ cation in the $\text{Cu}–\text{O}–\text{M}^{\text{III}}–\text{O}–\text{Cu}$ linkages.\cite{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, $\text{CuAlO}_2$ has received most of the attention. This has included investigating the band gap,\cite{25,26} intrinsic defects,\cite{27} doping to form acceptor levels,\cite{28} and doping for dilute magnetic semiconductor applications (both in the Cu position and the Al position).\cite{26,29}\text{CuAlO}_2$ was investigated by Nie \textit{et al.},\cite{26} along with $\text{CuInO}_2$ and $\text{CuGaO}_2$, 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,\cite{30} who investigated the hexagonal cell of $\text{CuAlO}_2$ 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 $\text{CuAlO}_2$ was also carried out by Hamada \textit{et al.}\cite{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 $\text{CuAlO}_2$. The effects of Cu and Al vacancies, and Be, Mg, and Ca dopants on the electronic structure of $\text{CuAlO}_2$ have also been investigated using LDA based LAPW calculations,\cite{28} with the results showing that the most promising defects for improving $p$-type conductivity are Cu vacancies and Be doping at Al sites.

$\text{CuScO}_2$ and $\text{CuYO}_2$ have received sparse attention, with only a handful of theoretical investigations in literature.\cite{30–33} Gilliland \textit{et al.}\cite{30} studied the band structure of $\text{CuScO}_2$ using LDA. They reported a direct band gap at $L$, but did not report the band gap magnitude.\cite{30} Shi and co-workers studied intrinsic\cite{31} and extrinsic\cite{32} defects in $\text{CuScO}_2$ and $\text{CuYO}_2$. 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 antisite becomes an important acceptor.\cite{31} Mg and Ca dopants are found to be the most prominent extrinsic defects.\cite{32} A recent study by Li and co-workers\cite{33} investigated the band edge features of $\text{CuM}^{\text{III}}\text{O}_2$ ($\text{M}^{\text{III}}=\text{Al}, \text{Y}, \text{Sc}, \text{Cr}$) and calculated the valence band alignment [valence band maximum (VBM)] of these materials to ascertain why $\text{CuScO}_2$ shows the best conductivity of the three. They found that $\text{CuScO}_2$ has the lowest hole effective mass and the highest VBM relative to the vacuum of all three, and concluded that these factors make $\text{CuScO}_2$ the most conductive.\cite{33}

$\text{CuCrO}_2$ 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.\cite{33,35} Our calculated simulated x-ray photoemission spectroscopy (XPS) for $\text{CuCrO}_2$ 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.\cite{35} Very recently, Eyert and co-workers\cite{36} investigated the electronic structure of $\text{CuCrO}_2$ 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 $\text{CuCrO}_2$ cell. This four atom cell cannot therefore take into account the antiferromagnetic (AF) nature of $\text{CuCrO}_2$,\cite{37} and hence this study is restricted to the higher energy ferromagnetic (FM) configuration.\cite{36} The PEDOS reports that Cr 3$d$ $t_{2g}$ states dominate at the top of the valence band, $\sim 1.5$ eV above the Cu 3$d$ peak,\cite{36} although this is inconsistent with high resolution XPS studies, which show that Cu states dominate at the VBM.\cite{35}

In this work, we systematically study the effect of the $\text{M}^{\text{III}}$ cation on the electronic structure and chemical bonding of $\text{CuM}^{\text{III}}\text{O}_2$ ($\text{M}^{\text{III}}=\text{Al}, \text{Y}, \text{Sc}, \text{Cr}$). We demonstrate the importance of the increased covalency between the $\text{M}^{\text{III}}$ 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.

\section{II. Calculation methodology}

Structural optimizations were performed on the hexagonal $\text{CuM}^{\text{III}}\text{O}_2$ (space group $P6_3/mmc$) cells using density functional theory (DFT).\cite{38,39} as implemented in the VASP
TABLE I. Structural data and nearest-neighbor interatomic distances for the optimized CuMIIIO2 (MII=Al, Cr, Sc, Y) structures. Percentage errors with respect to the experimental data [CuAlO2 (Ref. 22), CuCrO2 (Ref. 58), CuScO2 (Ref. 59), and CuYO2 (Ref. 60)] are given in parentheses. Volumes are given in Å³ and lattice dimensions and interatomic distances in Å.

<table>
<thead>
<tr>
<th></th>
<th>CuAlO2</th>
<th>CuCrO2</th>
<th>CuScO2</th>
<th>CuYO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume</td>
<td>81.79</td>
<td>92.50</td>
<td>104.47</td>
<td>125.90</td>
</tr>
<tr>
<td>a</td>
<td>2.885(+0.7%)</td>
<td>3.055(+2.9%)</td>
<td>3.248(+0.7%)</td>
<td>3.562(+1.1%)</td>
</tr>
<tr>
<td>c</td>
<td>11.340(+0.2%)</td>
<td>11.416(+0.1%)</td>
<td>11.429(+0.1%)</td>
<td>11.454(+0.1%)</td>
</tr>
<tr>
<td>Cu–O</td>
<td>1.866</td>
<td>1.844</td>
<td>1.832</td>
<td>1.821</td>
</tr>
<tr>
<td>MIII–O</td>
<td>1.928</td>
<td>2.032</td>
<td>2.138</td>
<td>2.306</td>
</tr>
</tbody>
</table>

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 MIII sizes. It has been suggested that the larger MIII cations can improve the capacity of a material for extrinsic doping on the MIII site, which can result in high hole concentrations,33 and this has been used to explain the more promising p-type conductivity of doped CuScO2 and CuYO2 compared to that of the smallest cation CuAlO2. This, however, does not explain the much higher p-type conductivity of Mg doped CuCrO2, considering it has a smaller MIII cation size than both CuYO2 and CuScO2. Nagarajan et al.21 suggested that a decrease in the cation MIII size, increases the Cu d-d overlap, resulting in greater conductivity. This would explain the trend in increasing conductivity for CuYO2 to CuSc2 to CuCrO2 but cannot explain the poor conductivity observed for CuAlO2.

B. Electronic structure

1. CuAlO2

The calculated band structure of CuAlO2 is shown in Fig. 2. The conduction band minimum (CBM) is positioned at $\Gamma$ and a broad, flat VBM is found along the H-K line and extends past K in the K-$\Gamma$ direction. This is in good agreement with previous calculations,36 but is at variance with the

III. RESULTS

A. Structure

The optimized structural parameters of CuMIIIO2 (MII=Al, Y, Sc, Cr) are shown in Table I. In all our delafossites,

FIG. 2. The electronic band structure of CuAlO2 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.
study by Robertson et al., 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, it has been proposed that intrinsic defect levels decrease the experimental value. A direct band gap of 3.1 eV is found at \( \Gamma \), compared to 3.5 eV found by experiment.

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. 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 2\( p \) in nature with a minor contribution from Al 3\( s \) and 3\( p \) states. Peak II is mainly O 2\( p \) although Cu 3\( d \) states are also present. Peak III is mostly Cu 3\( d \) with some O 2\( p \) 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 3\( d \) and O 2\( p \).

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 eV found near \( M \) along \( M-I \). 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\(_2\). The presence of two Cr sites introduces the possibility of magnetic ordering within the periodicity of the simulated unit cell. Due to the \( t_2g \) 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.

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. 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-
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 $\sim -2.5$ 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 2$p$ states dominate the lower valence band, with peaks I and II being made up mainly of O 2$p$ states, but with significant contributions from Cu 3$d$ and Cr 3$d$ states. The bottom of the conduction band is predominantly Cr in nature, with the contribution from O 2$p$ states now extending up to $\sim -5$ eV due to increased interaction with the Cr 3$d$. 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 $\Gamma$.

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 $\Gamma$. Previous studies by Shi et al.\textsuperscript{33} and Gilliland et al.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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 3$d$ states between $-4$ and 0 eV, but also features some 3$d$ 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 3$d$ 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 2$p$ in nature with some interaction with Cu 3$d$, peak III is of mainly O 2$p$ character with some signifi-

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 $\Gamma$, giving an indirect band gap of 2.93 eV, which is consistent with the work of Shi et al.,\textsuperscript{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. 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.

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.

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

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 Bader partial charge analysis.

The calculated Bader charges are listed in Table II. Al 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, −1.06e for Cr, and −1.27e 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

\[
\frac{1}{m^*(E)} = \frac{1}{\hbar^2} \frac{dE}{dk},
\]

where E(k) is the band edge energy as a function of wave vector k, obtained directly from the GGA+U calculation.
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 [010] direction, with the effective mass of CuAlO\(_2\) 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 CuAlO\(_2\) at the valence band edge. Surprisingly, the delafossite with the smallest effective mass in the [001] direction is CuYO\(_2\). This is at variance with the results of Shi et al., who found that the effective masses of CuScO\(_2\) were lower than that of CuYO\(_2\) and CuAlO\(_2\). This, however, is based on the average of the effective masses in the three directions.\(^{33}\) Indeed, the effective mass of CuYO\(_2\) in the [001] direction is found to be lower than that for CuScO\(_2\) and CuAlO\(_2\), meaning CuYO\(_2\) should find it easiest to conduct along the O−Cu−O chain.\(^{33}\) 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 CuAlO\(_2\)\(^{69}\), CuScO\(_2\)\(^{70}\), and CuYO\(_2\) (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\(^{III}\)O\(_2\) 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 CuYO\(_2\), CuScO\(_2\), and CuCrO\(_2\) are smaller than that of CuAlO\(_2\) and that, on the average, the effective masses for CuCrO\(_2\) 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)O\(_2\) (Ref. 26) and for Cu(Al/Sc/Y)O\(_2\).\(^{33}\) Although these are separate studies from different authors, the authors of the latter study used the approximate transitivity of the of band offsets\(^{74}\) to compare the alignments in both studies. They concluded that CuScO\(_2\) 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 \( 1 \times 1 \times 8 \) were constructed in the [001] direction, resulting in 48 and 64 atom superlattices made up of a 50-50 mix of CuAO\(_2\)/CuBO\(_2\). The lattice constants of CuAO\(_2\) and CuBO\(_2\) 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

\[
\Delta E_{\text{Va}} \text{ClA} = \Delta E_{\text{CuAO}2-\text{VBM-CL}} - \Delta E_{\text{CuBO}2-\text{VBM-CL}} + \Delta E_{\text{CuAO}2-\text{ClA}} - \Delta E_{\text{CuBO}2-\text{ClA}},
\]

where \( \Delta E_{\text{CuAO}2-\text{VBM-CL}} = E_{\text{CuAO}2-\text{VBM}} - E_{\text{CuAO}2-\text{CL}} \) and \( \Delta E_{\text{CuBO}2-\text{VBM-CL}} = E_{\text{CuBO}2-\text{VBM}} - E_{\text{CuBO}2-\text{CL}} \). These are the core level (CL) to VBM separations for pure CuAO\(_2\) and CuBO\(_2\) at their equilibrium lattice constants. \( \Delta E_{\text{CuAO}2-\text{ClA}} = E_{\text{CuAO}2-\text{ClA}} - E_{\text{CuBO}2-\text{ClA}} \) 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>
<thead>
<tr>
<th>Material</th>
<th>( m_{100} )</th>
<th>( m_{010} )</th>
<th>( m_{001} )</th>
<th>( m_{100} )</th>
<th>( m_{010} )</th>
<th>( m_{001} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAlO(_2)</td>
<td>2.60</td>
<td>2.60</td>
<td>58.43</td>
<td>2.60</td>
<td>2.60</td>
<td>38.95</td>
</tr>
<tr>
<td>CuCrO(_2)</td>
<td>2.96</td>
<td>2.96</td>
<td>7.21</td>
<td>4.53</td>
<td>4.53</td>
<td>6.07</td>
</tr>
<tr>
<td>CuScO(_2)</td>
<td>4.00</td>
<td>4.00</td>
<td>8.22</td>
<td>4.00</td>
<td>4.00</td>
<td>8.22</td>
</tr>
<tr>
<td>CuYO(_2)</td>
<td>4.21</td>
<td>4.21</td>
<td>7.16</td>
<td>3.72</td>
<td>3.72</td>
<td>7.64</td>
</tr>
</tbody>
</table>
TABLE IV. The GGA+U natural band alignments of CuM$^{\text{III}}$O$_2$ (M$^{\text{III}}$=Al, Sc, Cr, Y) calculated using the O 1s states; the Cu 1s states; the M$^{\text{III}}$ 1s; and the average of the Cu 1s, O 1s, and M$^{\text{III}}$ 1s states as the core levels (denoted {1s}). CuScO$_2$ is taken as the reference level in all four alignments.

<table>
<thead>
<tr>
<th></th>
<th>O 1s</th>
<th>Cu 1s</th>
<th>M$^{\text{III}}$ 1s</th>
<th>(1s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAlO$_2$</td>
<td>−0.01</td>
<td>+0.29</td>
<td>−1.52</td>
<td>−0.41</td>
</tr>
<tr>
<td>CuCrO$_2$</td>
<td>+0.07</td>
<td>+0.22</td>
<td>−0.63</td>
<td>−0.11</td>
</tr>
<tr>
<td>CuScO$_2$</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>CuYO$_2$</td>
<td>−0.016</td>
<td>−0.19</td>
<td>+1.05</td>
<td>+0.23</td>
</tr>
</tbody>
</table>

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 Cu(Al/In/Ga)O$_2$ used CLs which they did not specify and the study of Cu(Al/Sc/Y)O$_2$ used the average of the 1s levels of Cu, M$^{\text{III}}$, and O 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$^{\text{III}}$ 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–A 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.

IV. DISCUSSION

Since the first report of $p$-type transparent conductivity in the CuM$^{\text{III}}$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, CuM$^{\text{III}}$O$_2$, TCOs retain popularity as a viable platform for future high performance $p$-type TCO applications. In addition, delafossite structured materials have started to receive attention as potential electrodes in photoelectrochemical (PEC) water splitting, 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).

It is clear from our results that due to the polaronic nature of these Cu$^\text{I}$ oxides, 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 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, accurate band offsets for ternary delafossites do not seem possible using this method.

As delafossites and Cu$^\text{I}$ oxides, in general, are known to be polaronic, 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. The Cu–Cu distance (equal to the $a/b$ lattice constant) is determined by the size of the M$^{\text{III}}$ ion, which suggests that the conductivity will increase as the size of the M$^{\text{III}}$ 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. This would also explain why undoped CuAlO$_2$ has been reported to have a higher conductivity than both nondoped CuScO$_2$ and CuYO$_2$.

Unfortunately, conduction in these systems is more complex than simply stating that conductivity is inversely proportional to the M$^{\text{III}}$ 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$^{\text{III}}$ again playing a leading role. The size of the M$^{\text{III}}$ plays another role in determining the nondoped conductivity of these materials, as the larger the M$^{\text{III}}$ ion, the more oxygen interstitials the material can contain. This conceivably explains why CuYO$_2$ (Ref. 24) is reported to have a higher nondoped conductivity than CuScO$_2$. It cannot, however, explain why CuCrO$_2$ has a higher undoped conductivity even than CuAlO$_2$.

Similarly, as the size of the M$^{\text{III}}$ ion increases, so too does the ability to dope the material. 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$^{\text{II}}$ substitution in CuCrO$_2$, with $x=0.05$ being the limit for CuCr$_{1-x}$Mg$_x$O$_2$. Despite this, the conductivity of CuCrO$_2$:$\text{Mg}$ is much higher than that of CuScO$_2$:$\text{Mg}$ and CuYO$_2$:$\text{Ca}$, which should be able to contain a much higher dopant concentration. Electronic structure of the M$^{\text{III}}$ 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$^{\text{III}}$ 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$^{\text{III}}$ ions. The important requirements for good conductivity would appear to be (i) the M$^{\text{III}}$ ion not being overly large, and thus not limiting the hole hopping, leading to good nondoped conductivity; (ii) the M$^{\text{III}}$ ion having a favorable electronic structure, which can enhance the mobility of holes; and (iii) the M$^{\text{III}}$ 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$^{\text{III}}$ ion big enough to allow doping and small enough not to limit hopping.

V. CONCLUSION

The electronic structure and geometry of CuM$^{\text{III}}$O$_2$ (M$^{\text{III}}$=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. Badger analysis indicates that the covalent interactions between the trivalent metal and oxygen follow the trend Al$^3+$–Y$^3+$–Sc$^4+$–Cr$^{3+}$ with 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$^{\text{III}}$ ion and the O 2$p$ states determines the mobility and conduction in these delafossite type materials.

ACKNOWLEDGMENTS

This publication has emanated from research conducted with financial support of Science Foundation Ireland: PI Grant Nos. 06/IN.1/I29 and 06/IN.1/I29/EC07. We also acknowledge support from the HEA for the PTRLI programs IITAC (Cycle III) and e-INIS (CYCLE IV). All calculations were performed on the IITAC supercomputer as maintained by the Trinity Centre for High Performance Computing (TCHPC) and the Stokes computer, maintained by the Irish Centre for High-End Computing (ICHEC).

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