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Chemical bonding in copper-based transparent conducting oxides: CuMO_2 ($M = \text{In, Ga, Sc}$)

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Abstract

The geometry and electronic structure of copper-based p-type delafossite transparent conducting oxides, CuMO_2 ($M = \text{In, Ga, Sc}$), are studied using the generalized gradient approximation (GGA) corrected for on-site Coulomb interactions (GGA + U). The bonding and valence band compositions of these materials are investigated, and the origins of changes in the valence band features between group 3 and group 13 cations are discussed. Analysis of the effective masses at the valence and conduction band edge explains the experimentally reported conductivity trends.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the modern electronics industry there is an increasing demand for transparent conducting oxides (TCOs) for use in numerous applications in devices such as solar cells, flat panel displays and light emitting diodes [1]. TCOs typically have optical band gaps greater than 3.1 eV to ensure transparency to visible light, and possess carrier concentrations of at least 10^{20} cm^{-3} [2]. However, although many successful n-type TCOs have been discovered (e.g. In_2O_3 [3], ZnO [4], SnO_2 [5]), there is a distinct lack of successful p-type materials which are required for the development of transparent p–n junctions for ‘invisible electronics’ [6].

The difficulty in developing high performance p-type TCOs stems mainly from the valence band make-up of most wide band gap oxides, which are typically dominated at the valence band maximum (VBM) by O 2p states. In order to successfully achieve p-type doping it is necessary to introduce holes into these systems, which effectively means oxidizing oxygen. These corresponding ‘oxygen holes’ are strongly localized polarons situated on single oxygen ions, coupled to strong lattice distortions [7, 8] and thus cannot migrate through the crystal, resulting in extremely poor p-type conduction. Another stumbling block is that the majority of these wide band gap oxides are natively n-type, which means that excess n-type

defects will effectively serve as hole ‘killers’ [9]. However, by alloying with a suitable cation, the O 2p states can be hybridized with cation d states so that the top of the valence band becomes more disperse. Introduction of holes into this type of system results in less localized holes allowing for higher mobilities, and hence p-type conductivity can be improved [10].

The first successful p-type TCO of this kind was CuAlO_2 which has the delafossite structure [11]. The delafossite structure consists of close-packed layers of Cu atoms which are linearly coordinated to two oxygen atoms to form O–Cu–O dumb-bells parallel to the crystallographic c -axis (figure 1). Each oxygen then coordinates to three metal ions forming layers of metal-centred octahedra parallel to the ab -plane. The delafossite structure can occur with a rhombohedral (space group $R\bar{3}mh$) or hexagonal (space group $P6_3/mmc$) unit cell depending on the stacking of the Cu ions with the hexagonal structure having ABAB packing while the rhombohedral structure has ABCABC packing [12]. Further investigations found that other Cu-based delafossite oxides also possessed p-type TCO ability, e.g. CuInO_2 , CuGaO_2 and CuScO_2 which have optical gaps of 3.9 eV [13, 14] 3.6 eV [15] and 3.3 eV [16] respectively.

Although n-type TCOs have been produced with conductivities of $\sim 10^4 \text{ S cm}^{-1}$ [6], thus far the conductivity

Figure 1. The structure of the rhombohedral delafossite unit cell—the red (small dark grey) atoms are O, yellow (large light grey) are Cu and green (large dark grey) are metal atoms (In, Ga, Sc).

of these p-type materials remains quite low. CuScO_2 has the highest reported p-type conductivity of the delafossites considered here, namely 30 S cm^{-1} when Mg-doped [17]. The conductivity of CuGaO_2 films is much lower with a conductivity of 1 S cm^{-1} achieved through Fe-doping [17]. Although CuInO_2 is a promising candidate TCO for p–n junctions due to its bipolar dopability [18], so far its conductivity remains very low, with n-type doping with Sn resulting in a conductivity of 0.0038 S cm^{-1} while a conductivity of 0.0028 S cm^{-1} has been reported for p-type Ca-doped films [13].

The conductivities of the three delafossites considered here (CuGaO_2 , CuInO_2 and CuScO_2) are considerably lower than that of Mg-doped CuCrO_2 , which is reported to possess the highest conductivity (220 S cm^{-1}) of all the delafossite oxides [19]. There have been many discussions in the literature about the influence of the size and electronic structure of the trivalent metal cation on conductivity [19–21]. Delafossites and Cu^{I} oxides in general are considered to be polaronic [22–36], and as such it is expected that the Cu–Cu

distances should play a part in any conductivity, with holes expected to hop from Cu to Cu [36]. The Cu–Cu distance (equal to the a lattice constant) is determined by the size of the M ion, which suggests that the conductivity will increase as the size of the M 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 non-doped conductivity [37]. This would also explain why undoped CuAlO_2 has been reported to have a higher conductivity than both undoped CuScO_2 and CuYO_2 [38].

Nagarajan *et al* attempted to explain the trend in increasing conductivity of $\text{CuY}_{1-x}\text{Ca}_x\text{O}_2$ to $\text{CuSc}_{1-x}\text{Mg}_x\text{O}_2$ to $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ by noting that the increasing conductivity tracks a decreasing ionic radius of the M cation, and hence a decreasing lattice parameter in the Cu ion plane [19]. They suggest that this leads to increased Cu d orbital overlap and as a result better hole mobility. This size dependence theory can effectively be ruled out by the observed conductivity of $\text{CuAl}_{1-x}\text{Mg}_x\text{O}_2$, which at $4 \times 10^{-4} \text{ S cm}^{-1}$ has a much lower conductivity than that of $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ (220 S cm^{-1}), despite the ionic radius of Al being smaller than Cr [38].

Sleight and co-workers have also discussed the effect of the M ion on the mobility of holes in p-type delafossites [20]. The authors suggest 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–O–Cu linkages. The authors suggest that the higher conductivities observed for CuCrO_2 and CuFeO_2 may be due to favourable mixing with the 3d states on the M cation in the Cu–O–M–O–Cu linkages [20]. The number of hole carriers (introduced by intrinsic or extrinsic defects) in the system is also very important, with size of the M again thought to play an important role. The size of the M may determine the non-doped conductivity of these materials, as the larger the M ion, the more oxygen interstitials the material can contain [17, 20]. This is consistent with the reported undoped conductivity of CuYO_2 [20] being higher than CuScO_2 [39]. It cannot, however, explain why CuCrO_2 has a higher undoped conductivity even than CuAlO_2 [38].

As the size of the trivalent ion increases, it has been postulated that the ability to dope the material also increases [40]. 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. This does not take into account, however, that suitably sized dopants for most trivalent cations can be found. 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 $\text{CuCr}_{1-x}\text{Mg}_x\text{O}_2$ [41]. 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. Therefore, the electronic structure of the M ion must also play a prominent role in conductivity, if not the dominant role.

Recently, in a theoretical investigation of CuMO_2 ($\text{M} = \text{Al, Cr, Y, Sc}$) it was proposed that the Cr 3d states appear in the valence band of CuCrO_2 and mix with the O 2p, with this increased covalency in the system leading to increased hole mobility [21]. This analysis has been supported

by calculations on the p-type chemistry of CuAlO_2 [42] and CuCrO_2 [43] which show that the thermodynamic transition levels for the copper vacancy in CuCrO_2 are much shallower than for CuAlO_2 , which is primarily mediated by the increased covalency of the Cr d states with the Cu and O states in the valence band of CuCrO_2 . These studies also highlight the vital role of the trivalent cation in any p-type conductivity.

Several calculations of the electronic structure and defects in CuMO_2 ($M = \text{Sc, Ga, Al}$) have been performed [44–50, 40, 51–53]. Previous calculations of the electronic structure have indicated CuGaO_2 and CuInO_2 to have indirect fundamental band gaps [44, 48, 49, 46]. The conduction band minimum (CBM) was located at Γ in all calculations. However, the position of the VBM is less clear, with several calculations placing it at F [48, 49, 46], while a previous local density approximation (LDA) calculation using the linearized augmented plane wave (LAPW) method suggested the VBM to be on the F– Γ line near F [44]. CuScO_2 was found to have a direct band gap at L [40, 51]. One of the reasons for the observed p-type conductivity is thought to be due to the high energy VBM of these materials, with CuInO_2 demonstrating bipolar dopability due to its lower CBM [44]. Defect studies of both intrinsic and extrinsic defects have shown that, in general, acceptor-type defects are more stable than donor defects in these oxides, which is the reason for their p-type conductivity [47, 52, 53]. Either copper vacancies or oxygen interstitials may be responsible for intrinsic conductivity with both defects having low formation energies in CuGaO_2 and CuInO_2 [46, 53] while oxygen interstitials are thought to dominate in CuScO_2 [23].

Despite the large number of studies conducted on these three delafossite materials, a proper analysis of the chemical bonding and of the effect of the trivalent cations on the valence band structure of these materials has been lacking. Similarly, all of the previous studies on these materials have failed to take into account the poor description of the location of the Cu 3d states by standard DFT functionals. In this study we have carried out detailed electronic structure calculations of CuInO_2 , CuGaO_2 and CuScO_2 using the generalized gradient approximation (GGA) corrected for on-site Coulomb interactions. We provide insight into the reasons behind p-type conductivity in these materials through examination of their band structures and detailed analysis of the chemical bonding in the densities of states, together with calculated effective masses and Bader charges for these materials in order to understand the conductivity trends.

2. Computational methods

All calculations were performed using periodic density functional theory as implemented in the VASP code [54, 55]. A plane-wave basis set was used to represent the wavefunctions, with the projected augmented wave (PAW) [56, 57] method used to represent the interaction between the core electrons (Cu: [Ar], O: [He], In: [Kr], Ga: [Ar], Sc: [Ne]) and valence electrons. The GGA was applied to the exchange–correlation functional within the Perdew–Burke–Ernzerhof (PBE) [58] implementation using corrections for

Table 1. The calculated structural parameters for CuInO_2 , CuGaO_2 and CuScO_2 with deviation from experimental values [68–70] given in brackets. Lattice dimensions and interatomic distances are given in ångströms.

	CuInO_2	CuGaO_2	CuScO_2
a	3.36 (+2.1%)	3.02 (+1.6%)	3.24 (+0.9%)
c	17.48 (+0.5%)	17.25 (+0.4%)	17.14 (+0.3%)
Cu–O	1.84 (–0.2%)	1.86 (+0.5%)	1.83 (+0.1%)
M–O	2.22 (+2.0%)	2.02 (+1.2%)	2.14 (+0.8%)

on-site Coulomb interactions for strongly correlated systems (PBE + U) [59]. The validity of PBE + U and its improvement over the PBE functional have been demonstrated in its recent use to provide more accurate descriptions of localization in systems with n-type [60–63] and p-type [64, 65] polarons. A value of U of 5.2 eV was used for the Cu 3d states as it accurately reproduces the valence band photoemission spectra of Cu_2O , CuAlO_2 and CuCrO_2 [12, 66, 21].

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 [67]. This approach avoids the problems of Pulay stress and changes in basis set which can accompany volume changes in plane-wave calculations. Convergence with respect to k -point sampling and plane-wave energy cut off was checked, and for all systems a Monkhorst Pack k -point grid of $8 \times 8 \times 8$ and a plane-wave cutoff of 500 eV were found to be sufficient. Calculations were deemed to be converged when forces on atoms were less than $0.001 \text{ eV } \text{\AA}^{-1}$. Partial electronic density of states (PEDOS) calculations were carried out using spherical projections of $1.4 \text{ \AA}$ for Cu, Sc and O, $1.5 \text{ \AA}$ for In and $1.2 \text{ \AA}$ for Ga.

3. Structure of CuMO_2 ($M = \text{In, Ga, Sc}$)

The optimized structural parameters for each delafossite are shown in table 1. The calculated lattice parameters are in reasonable agreement with their experimental values [68–70] with increases in the a parameters of 2.1%, 1.6% and 0.9% for CuInO_2 , CuGaO_2 and CuScO_2 , respectively, while the c parameter shows a smaller increase of 0.3–0.5%. The Cu–O bond distance remains similar in all three structures, varying between 1.832 and 1.857 $\text{\AA}$, while the M–O distance varies depending on the metal, with In–O having the longest and Ga–O the shortest bond length.

4. Electronic structure

4.1. CuInO_2

The band structure of CuInO_2 is shown in figure 2. The valence band width is calculated as 6.2 eV. A large dispersion at the CBM is seen at Γ . This is due to the s-type nature of the CBM which is made up of 65% s states from mainly In and O at the Γ -point [71]. The lowest energy state in the conduction band is split off from the rest of the conduction band by 0.5 eV. The

Figure 2. Band structure of CuInO₂. The dashed line shows the valence band maximum (VBM). The highest occupied state (VBM) is set to 0 eV.

Figure 3. EDOS and PEDOS for CuInO₂. The vertical dashed line indicates the valence band maximum. The blue (dotted) line indicates s states, red (solid) p states and green (dashed) d states.

VBM occurs at F, while the CBM occurs at Γ making CuInO₂ an indirect gap semiconductor with a band gap of 0.57 eV. The position of the VBM differs from previous LAPW calculations which placed it on the Γ -F line near F [44]. The smallest direct gap occurs at Γ and has a value of 1.10 eV. This is an improvement on the band gap previously calculated through LDA calculations (direct gap of 0.73 eV) [44], though it is still underestimated from the experimental optical band gap of 3.90 eV [13, 14]. However, some of this discrepancy has been explained previously by optical absorption calculations which show direct Γ - Γ and Z-Z transitions to be forbidden in the delafossite structure, with absorptions only occurring at the F and L points [44]. The calculated band gaps at the F and L points are 4.13 eV and 3.89 eV, respectively, which show much better agreement with the experimental optical gap.

Figure 3 shows the total and partial electronic density of states (EDOS/PEDOS) for CuInO₂. In the simplest ionic model, the valence band is composed of a filled band of O 2p states below a filled band of Cu 3d states. Hence the bottom

Figure 4. Orbital-decomposed Cu 3d and O 2p PEDOS for CuInO₂. For the Cu 3d PEDOS, orange (light grey) solid and dashed lines indicate Cu 3d_{xy} and 3d_{x²-y²}, blue (dark grey) solid and dashed lines indicate Cu 3d_{xz} and 3d_{yz}, and the green dotted line indicates Cu 3d_{z²} states. For the O 2p PEDOS, the red solid, dotted and dashed lines indicate O 2p_z, 2p_y and 2p_x states, respectively.

of the valence band results from weak bonding interactions between mainly O 2p states with only small contributions from Cu 3d states, while the upper part of the valence band results from weak antibonding interactions between mainly Cu 3d states with only small O 2p contributions. O 2p states dominate the valence band between -6.9 and -2.5 eV with a small amount of mixing with In 5s states around -6.4 eV. From -2.5 to -1.8 eV Cu 3d states dominate, while from -1.8 eV to the VBM there is a significant admixture of O 2p and Cu 3d states. The CBM is made up of a mixture of Cu 3d states, In 5s and 5p states and O 2p and 2s states.

The valence band composition can be understood by decomposing the Cu 3d and O 2p states into their component orbitals as shown in figure 4. Three major peaks are seen for the Cu 3d orbitals centred around -2.2 eV (d_{xy} and d_{x²-y²}), -1.5 eV (d_{yz} and d_{xz}) and -0.5 eV (d_{z²}). The O 2p orbitals show a number of peaks across the energy range with p_x and p_y orbitals possessing similar topography while the O p_z show a different trend.

The O-Cu-O bonds run along the crystallographic *c*-axis and the O 2p-Cu 3d interactions within these bonds can be divided into σ , π and non-bonding interactions depending on the symmetry of the atomic orbitals involved. The O p_z and Cu d_{z²} orbitals interact via strong σ -interactions, giving rise to a bonding interaction which is mainly O p_z with a small amount of Cu d_{z²} character at -6.4 eV (O p_x/p_y contributions to this peak occur due to In 5s interactions within the In-O bonds), and an antibonding interaction which is mainly Cu d_{z²} with a small amount of O p_z character at -0.5 eV. π -interactions between the O p_x/p_y and Cu d_{yz}/d_{xz} orbitals result in significant mixing of these states with the O p_x/p_y states dominating the bonding interaction centred around -4.0 eV

Figure 5. Band structure of CuGaO₂. Dashed line indicates the valence band maximum which is set at 0 eV.

and the Cu d_{yz}/d_{xz} dominating the antibonding interaction at -1.5 eV. Finally the Cu $3d_{xy}$ and $3d_{x^2-y^2}$ states around -2.2 eV are of non-bonding character as they are of σ -symmetry and cannot interact strongly with the O $2p$ states.

4.2. CuGaO₂

Figure 5 shows the band structure of CuGaO₂ which appears topographically similar to that of CuInO₂. The valence band width is slightly larger than for CuInO₂ at 7.4 eV with the lowest energy band separated from the rest of the valence band by 0.6 eV at L. A large dispersion is again seen at the CBM due to the interaction between s states from Ga and O atoms. The VBM occurs at F and the CBM occurs at Γ , indicating CuGaO₂ to be an indirect gap semiconductor as found previously [44, 46, 49]. The calculated indirect band gap is 1.16 eV, while the band structure also shows a larger direct gap at Γ which is calculated as 2.08 eV compared to the experimental optical gap of 3.6 eV [15]. Again because Γ - Γ and Z-Z transitions have been found to be symmetry-forbidden [44], the direct gaps at F and L of 3.94 eV and 3.49 eV, respectively, show much better agreement with experimental data.

The total and partial EDOS for CuGaO₂ are shown in figure 6. Similar to CuInO₂, the valence band is made up of a mixture of Cu $3d$ and O $2p$ states. The lower part of the valence band between -8.0 and -3.0 eV is composed of mainly O $2p$ states with some hybridization between Ga $4s$ states at -7.3 eV. Cu $3d$ states dominate between -3.0 and -1.8 eV, while in the upper valence band between -1.8 eV and the VBM, a mixture of O $2p$ and Cu $3d$ states is seen. The CBM is made up of a mixture of Cu $3d$ and $4s$, Ga $4s$ and O $2s$ and $2p$ states.

Following a similar analysis as for CuInO₂, breaking down the O $2p$ and Cu $3d$ states into their component orbitals (figure 7) helps to explain the peaks in the total DOS. σ -interactions between O p_z and Cu d_{z^2} states lead to a bonding state at the bottom of the valence band at 7.3 eV of mainly O p_z character and an antibonding state at the top of the valence band at -0.5 eV of mainly Cu d_{z^2} character. O p_x/p_y contributions at -7.3 eV occur due to mixing with Ga s states. Significant mixing between O p_x/p_y and Cu d_{xz}/d_{yz} states occurs due to π -interactions, which lead to a bonding interaction dominated by O p_x/p_y states at -3.5 eV

Figure 6. EDOS and PEDOS for CuGaO₂. The vertical dashed line indicates the valence band maximum. The blue (dotted) line indicates s states, red (solid) p states and green (dashed) d states.

Figure 7. Orbital-decomposed Cu $3d$ and O $2p$ PEDOS for CuGaO₂. For the Cu $3d$ PEDOS, orange (light grey) solid and dashed lines indicate Cu $3d_{xy}$ and $3d_{x^2-y^2}$, blue (dark grey) solid and dashed lines indicate Cu $3d_{xz}$ and $3d_{yz}$, and the green dotted line indicates Cu $3d_{z^2}$ states. For the O $2p$ PEDOS, the red solid, dotted and dashed lines indicate O $2p_z$, $2p_y$ and $2p_x$ states, respectively.

and an antibonding interaction dominated by Cu d_{xz}/d_{yz} states at -2 eV. The Cu d_{xy} and $d_{x^2-y^2}$ states at -2.7 and -2.2 eV are of σ -symmetry and do not interact significantly with O $2p$ states.

4.3. CuScO₂

The band structure of CuScO₂ is shown in figure 8. The valence band width at 6.0 eV, is smaller than for both CuInO₂

Figure 8. Band structure of CuScO₂. The dashed line indicates the valence band maximum.

Figure 9. EDOS and PEDOS for CuScO₂. The vertical dashed line indicates the valence band maximum. The blue (dotted) line indicates s states, the red (solid) p states and the green (dashed) d states.

and CuGaO₂ and the CBM no longer shows a high dispersion at Γ . This is due to the differing nature of the states at the CBM. Both CuInO₂ and CuGaO₂ have CBMs composed of hybridized In/Ga s states and O 2s states, whereas CuScO₂ has a conduction band which is of mainly Sc 3d character (figure 9). It is the interaction between the metal s states which results in a highly dispersed conduction band in CuInO₂ and CuGaO₂ [72]. As the conduction band of CuScO₂ is composed of mainly Sc 3d states which do not interact as strongly due to their more localized nature, the dispersion is lessened. Both the VBM and CBM occur at L, indicating CuScO₂ to be a direct gap semiconductor as shown previously [40, 51] with a band gap of 2.84 eV, slightly underestimated from its experimental value of 3.3 eV [16]. As this transition is symmetry-allowed [40], better agreement between calculated and experimental values is seen compared to CuInO₂ and CuGaO₂. The indirect gap between the CBM at Γ and the VBM at L is very close in energy at only 2.88 eV. The location of the smallest direct gap at L is in contrast to CuInO₂ and CuGaO₂, which both have their smallest direct gap at Γ due to the s-type character of the CBM.

Figure 10. Orbital-decomposed Cu 3d and O 2p PEDOS for CuGaO₂. For the Cu 3d PEDOS, orange (light grey) solid and dashed lines are Cu 3d_{xy} and 3d_{x²-y²}, blue (dark grey) solid and dashed lines are Cu 3d_{xz} and 3d_{yz}, and the green dotted line indicates Cu 3d_{z²} states. For the O 2p PEDOS, the red solid, dotted and dashed lines indicate O 2p_z, 2p_y and 2p_x states, respectively.

The calculated total and partial EDOS for CuScO₂ are shown in figure 9. Similar to the DOS for CuInO₂ and CuGaO₂, the valence band is again composed of mainly Cu 3d and O 2p states. The lower valence band between -6.0 and -2.5 eV is dominated by O 2p states with only a small contribution from Cu 3d states. Between -2.5 and -1.5 eV Cu 3d states dominate with little contribution from O 2p states while the upper part of the valence band from -1.5 eV to the VBM is composed of a mixture of Cu 3d states and O 2p states. In contrast to the previous delafossites examined, the conduction band of CuScO₂ is dominated by Sc 3d states with a small amount of hybridization between O 2p states. Two bands are seen, one centred around 4.5 eV and the second centred around 6.5 eV.

Figure 10 shows the orbital-decomposed Cu 3d and O 2p states in the valence band. The O 2p states show three distinct peaks in the lower valence band due to bonding interactions, while in the upper valence band the Cu 3d states show three major peaks due to antibonding interactions. σ -interactions between Cu d_{z²} and O p_z lead to the mainly O p_z state at -5.5 eV and the Cu d_{z²} state at -0.4 eV. π -interactions between O p_x/p_y and Cu d_{xz}/d_{yz} lead to the O p_x/p_y dominated state at -4.0 eV and the Cu d_{xz}/d_{yz} state at -1.3 eV, while the d_{xy}/d_{x²-y²} states at -2.1 and -2.3 eV are of non-bonding character.

5. Bader charges

Table 2 shows the calculated Bader [73–75] charges for each delafossite considered. The Cu charges in all three materials are similar, with calculated values of 0.50 for CuInO₂, 0.53

Table 2. Calculated Bader charges for CuInO₂, CuGaO₂ and CuScO₂.

	CuInO ₂	CuGaO ₂	CuScO ₂
Cu	0.50	0.53	0.51
M	1.83	1.88	2.03
O	-1.17	-1.20	-1.27

for CuGaO₂ and 0.51 for CuScO₂. This compares to a charge of +1 for Cu in a fully ionic model indicating copper to be quite covalent in all compounds. CuInO₂ and CuGaO₂ show similar oxygen charges of -1.17 and -1.20, respectively, while CuScO₂ shows a slightly more negative charge of -1.27 indicating greater ionicity in CuScO₂. Examining the metals, In, Ga and Sc have charges of 1.83, 1.88 and 2.03, respectively. These are all less than the +3 charge expected; however, the ionicity of the metals differs between the three compounds with In the least and Sc the most ionic.

The Bader charges suggest that although all of the delafossites considered possess a high degree of covalency both in Cu–O and M–O bonding, as was also seen from the amount of hybridization in the PEDOS, the degree of covalency differs, with covalency increasing from CuScO₂ to CuGaO₂ to CuInO₂. It could be expected that the compound with the highest degree of covalency would show the greatest conductivity as it should possess the greatest hybridization between O 2p and Cu 3d states in the valence band. In fact, the experimental conductivity trend is opposite to the trend in covalency. Thus covalency cannot be used to rationalize the conductivity trend in these delafossites.

6. Effective mass

As these delafossites are all p-type conductors they should all have a low effective mass at the VBM which allows for greater mobility for carrier transport. Conversely n-type conductors should have a low effective mass at the CBM. We have calculated the transport effective mass, m_T^* at the VBM and CBM of each delafossite [76] using

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

where E is the band edge energy as a function of the wavevector k which is obtained from the PBE+ U calculations. This assumes that the first derivative of E is the same as that of a parabolic band at the same k -point. However, as the valence band maxima of the delafossites considered in this study are not parabolic, and these materials are thought to conduct through a polaronic hopping mechanism rather than a band conduction mechanism [22–24, 36, 77, 78], the calculated masses are not completely accurate and are merely used to provide insight into the conducting properties of these materials. Table 3 shows the calculated effective masses at the VBM and CBM for each compound. The effective masses for the VBM and CBM of CuInO₂ and CuGaO₂ were calculated at F and Γ , respectively, while those for CuScO₂ were both calculated at L. The VBM effective masses for p-type conductivity for CuInO₂ and CuGaO₂ were found to be

Table 3. Effective masses at the VBM and CBM for CuGaO₂, CuInO₂ and CuScO₂.

	Material	Point	m_{100}	m_{010}	m_{001}
VBM	CuInO ₂	F ($\frac{1}{2}, \frac{1}{2}, 0$)	3.22	3.22	0.68
	CuGaO ₂	F ($\frac{1}{2}, \frac{1}{2}, 0$)	2.04	2.04	0.58
	CuScO ₂	L ($0, \frac{1}{2}, 0$)	3.12	0.45	3.12
CBM	CuInO ₂	Γ (0, 0, 0)	0.37	0.37	0.37
	CuGaO ₂	Γ (0, 0, 0)	0.42	0.42	0.42
	CuScO ₂	L ($0, \frac{1}{2}, 0$)	1.08	0.56	1.08

isotropic in the [100] and [010] directions with the lowest effective masses occurring in the [001] direction of $0.68m_0$ and $0.58m_0$, respectively. CuScO₂ has a VBM effective mass which is isotropic in the [100] and [001] directions, with the lowest effective mass in the [010] direction of $0.45m_0$. The difference in the direction of the lowest effective mass is due to the VBMs in CuInO₂/CuGaO₂ occurring at F while CuScO₂ has its VBM at L. We have also calculated the effective masses along the high symmetry directions and found that CuInO₂ possesses a lower effective mass of $0.58m_0$ in the F– Γ direction and CuGaO₂ has a lower effective mass of $0.46m_0$ also in the F– Γ direction. The VBM effective mass data thus follow the experimental p-type conductivity trend with CuScO₂ having the lowest calculated effective mass and the highest reported conductivity [16, 20], while CuInO₂ has the lowest reported conductivity [17] of the compounds and the largest effective mass.

As CuInO₂ can be bipolar doped, it is of interest to examine the conduction band effective mass for each compound to determine its electron effective mass for n-type conductivity. For CuInO₂ and CuGaO₂ the effective masses were found to be isotropic in the [100], [010] and [001] directions with values of $0.37m_0$ and $0.42m_0$, respectively. The CBM effective mass for CuScO₂ was found to be anisotropic with the smallest effective mass in the [010] direction of $0.56m_0$. The calculated effective masses along the high symmetry directions showed CuGaO₂ to have a lower effective mass of $0.33m_0$ along Γ –Z and an effective mass of $0.41m_0$ along Γ –F, while CuInO₂ has a calculated effective mass of $0.38m_0$ and $0.37m_0$ along Γ –Z and Γ –F, respectively. CuScO₂ was found to have effective masses of $1.08m_0$ and $1.05m_0$ along L–F and L–Z, respectively. The high effective masses found for CuScO₂ relative to CuInO₂ and CuGaO₂ is not unexpected given the lesser dispersion at the CBM in its band structure. Although both CuGaO₂ and CuInO₂ have low conduction band effective masses, only CuInO₂ has thus far shown n-type dopability. This is due to its lower CBM relative to CuGaO₂ [44].

7. Discussion

In agreement with the conclusions of Nie *et al* [44], we find that for the group 13 delafossites the size of the direct band gap decreases with increasing atomic number in going from Ga (2.08 eV) to In (1.10 eV). This is the reverse of the trend in experimental optical band gaps which are 3.6 eV for

CuGaO₂ and 3.9 eV for CuInO₂ [13–15]. Transitions from the VBM to the CBM of CuScO₂ are symmetry-allowed [40], however, meaning that the minimum calculated band gap of 2.84 eV at L corresponds to the optical band gap of 3.3 eV seen experimentally [16]. If we take into account that Γ – Γ and Z – Z transitions are symmetry-forbidden [44] for CuInO₂ and CuGaO₂ and instead examine the symmetry-allowed direct gap at F and L, much better agreement with experiment is seen and the optical gap increases with atomic number with the minimum symmetry-allowed transition at L going from 2.84 eV in CuScO₂ to 3.49 eV in CuGaO₂ to 3.89 eV in CuInO₂. Although CuInO₂ and CuGaO₂ were both found to be indirect gap semiconductors with their VBMs at F and CBMs at Γ , CuScO₂ was found to be a direct gap semiconductor which is more favourable for its use in optoelectronic applications due to the greater efficiency in absorption/emission in direct gap semiconductors [79].

All of these materials were found to have valence bands made up of a mixture of Cu 3d and O 2p states, with the bonding interactions resulting in a lower valence band of mainly O 2p states and antibonding interactions giving rise to an upper valence band of mainly Cu 3d character. The length of the Cu–O bond has quite a large effect on the electronic structure of these oxides. Examining the π -interactions within the O–Cu–O bonds in the valence band PEDOS (figures 4, 7, 10) shows that CuGaO₂ has the smallest separation between the antibonding O p_x/p_y and bonding Cu d_{xz}/d_{yz} states (1.4 eV), CuInO₂ possesses a larger separation of 2.0 eV while CuScO₂ has a separation of 2.7 eV. This can be correlated with the Cu–O bond length in these materials. CuScO₂ has the shortest bond length (1.832 Å) and hence the greatest π -overlap between the O p_x/p_y and Cu d_{xz}/d_{yz} states resulting in the strongest interaction and widest separation between antibonding and bonding π -states of the three delafossites. CuInO₂ has a longer bond length of 1.841 Å giving rise to a slightly narrower separation, while CuGaO₂ has the longest bond length (1.857 Å), the weakest hybridization between O p_x/p_y and Cu d_{xz}/d_{yz} and hence the smallest separation. These considerations have recently been seen experimentally in x-ray emission spectroscopy (XES) studies [80].

The conductivity of the doped delafossites is experimentally known to increase from CuInO₂ to CuGaO₂ to CuScO₂ and our calculated effective masses show good correlation with this trend. Effective mass theory, however, is based on classical semiconductors with parabolic bands. Delafossites and Cu(I) based oxides in general have been thought to be polaronic in nature [36, 77, 78, 24, 22, 23, 33, 35, 81, 42], and therefore will not be well described within effective mass theory. A simple visual analysis of the dispersion at the VBM for all three delafossites reveals the flat nature of the bands, which will not be conducive to high performance p-type conductivity. It is thus not surprising that p-type Cu(I)-based TCOs based on the delafossite structure have continued to fail to live up to the expectations placed on them by the semiconducting and optoelectronic industries [2, 6, 82].

8. Conclusion

Using GGA corrected for on-site Coulomb interactions (GGA + U), the geometry and electronic structure of CuMO₂ (M = In, Ga, Sc) have been thoroughly investigated. A detailed analysis of the band structure and density of states explains the bonding and antibonding interactions between Cu 3d and O 2p states, which give rise to the valence band features of the delafossites and reveals the origins behind the observed differences between the valence band features of the group 13 and group 3 delafossites. Combining the electronic structure results with the calculated effective masses allows us to explain the experimental conductivity trends and explains why p-type conductivities in Cu-based delafossites remain too low for high performance TCO applications.

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