Comparative study of band structures in copper delafossites from x-ray emission spectroscopy

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Widespread interest in the electronic properties of ternary delafossite oxides of CuI with the general formula CuI\textsubscript{II}O\textsubscript{2} (where CuI\textsubscript{II}O\textsubscript{2} is a trivalent metal ion) has been prompted by the fact that these materials combine the properties of optical transparency in the visible region with a reasonable p-type conductivity. This leads to potential applications in "transparent oxide electronics" where the conductivity. This leads to potential applications in "transparent oxide electronics" where the conductivity of measured optical gaps is found in the group 3 series CuI\textsubscript{II}O\textsubscript{2} > CuGaO\textsubscript{2} > CuInO\textsubscript{2}. The last of these compounds is of particular interest as it is amenable to bipolar doping. More recently CuScO\textsubscript{2} (Ref. 8) and CuCrO\textsubscript{2} (Refs. 9–12) have emerged as alternative p-type TCOs: the highest conductivity in any p-type TCO is found in Mg-doped CuI\textsubscript{II}O\textsubscript{2}. Somewhat surprisingly the optically measured band gaps in the group 13 delafossites follow the sequence CuAlO\textsubscript{2} > CuGaO\textsubscript{2} > CuInO\textsubscript{2} > CuScO\textsubscript{2}. In the present Brief Report we present XPS and XES allow us to establish that as for CuAlO\textsubscript{2} and CuCrO\textsubscript{2} the upper part of the valence band is composed of O 2p orbitals of dominant Cu 3d\textsubscript{xy} orbital character whereas states in the valence band are of dominant Cu 3d\textsubscript{atomic} character but with significant mixing with O 2p states.

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Ga₂O₃ (Aldrich 99.99%) and Cu₂O (Aldrich 99.99%) under flowing argon at 1100 °C for 24 h. The sample was then pressed into pellets between tungsten carbide dies and refired as above for a further 24 h. The x-ray diffraction pattern of the product was characteristic of the 3R phase. CuScO₂ was prepared by firing a pelletized mixture of CuO and Sc₂O₃ in air at 1100 °C for 24 h, followed repelletization and refiring at 1100 °C for a further 24 h. The samples were quenched from 1100 °C by dropping into liquid nitrogen to prevent oxidation. Phase pure 2H material was obtained by using a 1% excess of CuO, as described by Kykyneshi et al.²⁴ CuInO₂ was prepared by pulsed laser deposition from a CuIn₂O₅ target under an oxygen ambient with pO₂=5×10⁻³ mbar, as described in detail elsewhere.²⁵ Samples for the photoemission study were prepared using a low level (2%) of Eu doping, which helped eliminate problems due to sample charging. High-resolution Al Kα x-ray photoemission spectra excited at hν=1486.6 eV were measured in a Scienta ESCA 300 spectrometer. The effective instrument resolution was 400 meV. Samples were cleaned in situ by annealing at 400 °C which reduced the C 1s to O 1s intensity ratio to below 1/100. Binding energies are referenced to the Fermi energy of a silver sample regularly used to calibrate the spectrometer.

X-ray emission spectra were measured on beamline 7.0.1 at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. This beamline is equipped with a spherical grating monochromator. Emission spectra were recorded using a Nordgren-type grazing-incidence spherical grating spectrometer. The beamline was set to have an energy resolution of 500 meV at the O K edge and the emission spectrometer was set to have a resolution of 350 meV. The O K emission spectra were calibrated relative to Zn L₁,₂ emission lines of Zn metal in second order.

O K-shell x-ray emission spectra of CuGaO₂, CuInO₂, and CuScO₂ are shown in the left-hand panels of Fig. 1: the right-hand panels show the corresponding O 2p partial densities of states (DOSs) derived from density-functional theory calculations. Decay of the O 1s core hole is governed by a strict dipole selection rule which only allows transitions from states with O 2p character. Thus the spectra provide a faithful measure of the O 2p partial density of states. In each case the spectra are dominated by a strong central peak labeled II in the figure with weaker features I and III to high and low photon energy, respectively. It can be clearly seen that there is a progressive decrease in the width of the valence band in the experimental spectra following the sequence CuGaO₂ > CuInO₂ > CuScO₂. The available experimental data for the delafossites are summarized in Fig. 2(a) where the experimental bandwidths are compared with results from density-functional theory calculations. The figure also include the calculated bandwidth for CuBO₂.²⁶ There is very good qualitative agreement between theory and experiment although the measured bandwidths are systematically bigger than in the calculations. Discrepancies of this type are a well-known problem when comparing the results of DFT with experimental data. Somewhat surprisingly there is a direct (rather than inverse) correlation between the overall width of the valence band and the calculated Cu-O bond length. However as shown in Fig. 2(b) there is an inverse correlation between the Cu-O and T-O bond lengths and the bandwidth therefore increases as the T-O bonds become shorter.
The pattern of intensities found in the x-ray emission spectra changes completely in x-ray photoemission spectra as seen in Fig. 3, where data for CuInO$_2$ are presented: the other delafossites showed very similar changes and the data are not presented here. The maximum intensity is now found at the top of the valence band with the peak about 2.7 eV below the band edge. This does not correspond to the maximum of peak I in the x-ray emission spectrum where the peak is found about 1.9 eV below the Fermi energy. We therefore label the peak maximum in XPS as I': the structure corresponding to the XES peak appears as a low binding energy shoulder to this peak. The intensity changes arise because XPS is determined by the cross-section weighted density of states that is a sum of atomically projected partial densities of states with each contribution weighted by a one electron ionization cross section. The total density of states is derived mainly by contributions from O 2$p$ and Cu 3$d$ states but the cross section for ionization of Cu 3$d$ states with Al K$\alpha$ radiation is a factor of 20 bigger than the O 2$p$ cross section.\cite{27} Thus the overall photoemission is dominated by the Cu 3$d$ contribution, as shown in the lower panel to Fig. 3. The changes between XES and XPS thus demonstrate that the states in the upper part of the valence band which give rise to peaks I and I' are of dominant Cu 3$d$ character, whereas the states in the bottom half of the valence band associated with II and III are of dominant O 2$p$ character. The nonvanishing intensity of I in O K-edge x-ray emission spectroscopy is a direct consequence of hybridization between Cu 3$d$ and O 2$p$ states arising from $\sigma$ and $\pi$ overlap within the O-Cu-O dumbbells. Conversely most of the intensity of peaks II and III in XPS arises not from the O 2$p$ states themselves but from the hybridization of Cu 3$d$ states with the O 2$p$ states in the bottom half of the valence band. The energy shift between peaks I and I' arises from the fact that the latter is associated with nonbonding Cu 3$d$ states of $\delta$ symmetry within the linear O-Cu-O units. Unlike the $\sigma$ and $\pi$ states, the $\delta$ states cannot hybridize with O 2$p$ states\cite{18,28} and so do not appear in XES. These ideas are illustrated in Fig. 4 where the Cu and O partial densities of states in the top half of the valence band are decomposed into components with local $\delta$, $\pi$, and $\sigma$ symmetry.\cite{20} The peak maximum in XPS coincides with Cu $\delta$ states and $\pi$ and $\sigma$ states appear as low binding-energy shoulders. By contrast there is near zero O $\delta$ amplitude across the whole of the valence band.

In summary we have used new XES measurements to compare bandwidths in the delafossite oxides CuGaO$_2$, CuInO$_2$, and CuScO$_2$ with that in CuAlO$_2$. The overall sequence we have found is CuAlO$_2$ > CuGaO$_2$ > CuInO$_2$ > CuScO$_2$, in agreement with recent calculations.\cite{20} The direct correlation between bandwidth and Cu-O bond length is found despite the fact that $\pi$ interactions are stronger the shorter the bond and the separation between O 2$p_{\pi}$ states and Cu 3$d_{xz/yz}$ states is greatest in CuScO$_2$. However in the main group delafossites the position of the bottom of the valence band is determined by hybridization with valence s states of the group 13 element and the extent of this hybridization decreases on descending the group. This reduces the competition with hybridization between Cu 3$d$ and O 2$p$ $\sigma$ states, allowing the Cu-O bond to contract but at the same time leading to a reduction in the overall width of the va-
lence band. There is very little contribution from Sc 4s states in CuScO$_2$ and the valence band is narrow. The increase in Cu-O bond length in moving across the transition series to CuCrO$_2$ arises from pronounced hybridization between Cr 3d and O 2p states across the entire valence band in this compound.

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