

The electronic structure of SrCu₂O₂ studied by synchrotron radiation excited photoemission and hybrid exchange density functional calculations

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Abstract

Photoemission spectra of K-doped SrCu₂O₂ excited with vacuum ultraviolet synchrotron radiation have been measured over a range of photon energies between 36 eV and 164 eV. Intensity changes in the spectra with changing photon energy show that the states at the top of the valence band are of dominant Cu 3d atomic character, although there is evidence for significant hybridisation between O 2p and Cu 3d states. The experimental results are compared with partial densities of states derived from calculations using a hybrid exchange approximation to density functional theory.

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Established transparent conducting oxides such as SnO₂, In₂O₃ or ZnO are all n-type materials [1] and there now appears to be little prospect of doping them p-type [2–4]. Exploitation of transparent conducting oxides in electronic and optoelectronic devices such as UV diodes will only become possible if suitable widegap oxides that can be doped p-type become available. A new family of p-type conducting ternary Cu(I) oxides that are transparent in the visible region has therefore aroused widespread interest. The first material of this sort was CuAlO₂ [5,6] followed later by CuGaO₂ [7] and CuInO₂ [8,9]. These delafossite oxides all have low energy *indirect* band gaps [10], limiting their potential usefulness in optoelectronic devices. By contrast the ternary oxide SrCu₂O₂ has a *direct* band-gap of around 3.3 eV [11,12] and a UV-emitting heterojunction was recently fabricated using p-type SrCu₂O₂ and n-type ZnO [13,14]. Thus the electronic structure of SrCu₂O₂ and the nature of the hole charge carriers are topics of major current interest.

In the simplest ionic model description SrCu₂O₂ is a d¹⁰ Cu(I) oxide with an upper valence band of filled Cu 3d states that sits above a band of filled O 2p states. The conduction band is derived from empty Cu 4s states. The structure of SrCu₂O₂ is based on planar zig-zag chains running in orthogonal [100] and [010] directions. Within the linear O–Cu–O units the Cu 3d_{z²} orbitals have σ -like symmetry, the 3d_{xz} and 3d_{yz} π -like symmetry and the 3d_{xy} and 3d_{x²-y²} δ -like symmetry. Thus O 2p orbitals can mix with Cu 3d_{z²} via strong σ overlap and with 3d_{xz} and 3d_{yz} via weaker π interactions. However 3d_{xy} and 3d_{x²-y²} must remain localised on Cu as there are no orbitals on oxygen of the correct δ symmetry for covalent mixing. Provided that the oxygen stoichiometry is unchanged, introduction of singly charged K⁺ onto Sr²⁺ sites must be accompanied formally by oxidation of a corresponding number of the Cu⁺ ions present in the lattice to Cu²⁺. Of course this introduces holes into the previously full Cu 3d bands. An issue of particular importance is the extent to which the Cu 3d and O 2p states mix, especially at the top of the valence band: it has been suggested that delocalisation of hole states off copper and onto oxygen by O 2p/Cu 3d

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hybridisation at the top of the valence band is a prerequisite for good hole mobility. In the present Letter, we present a photoemission study of K-doped SrCu_2O_2 using a range of photon energies between 36 eV and 158 eV to excite the spectra. Changes in relative intensities of spectral features with varying photon energy allow us to distinguish between O 2p and Cu 3d states and also provide for the first time a direct experimental probe of the extent of hybridisation between the cation and anion states. The experimental results are compared with calculations of the electronic structure performed using hybrid exchange density functional theory. In contrast to previous computational studies [12,15] we are able to calculate a value for the bulk bandgap in quantitative agreement with the experimental value.

The tetragonal structure of SrCu_2O_2 belongs to the space group I 41/AMD with a unit cell containing two formula units and defined by the lattice constants $a = 5.469 \text{ \AA}$ and $c = 9.826 \text{ \AA}$. The calculations presented have been performed using the CRYSTAL06 software [16]. Electronic exchange and correlation were approximated using the hybrid exchange formalism which has previously been demonstrated to provide a reliable description of the ground state electronic structure in copper oxides [17] and, of particular relevance to the current study, of the nature and value of the band gap in a wide variety of materials [18]. The most significant numerical approximation is the expansion of the crystalline orbitals in a basis set consisting of a linear combination of atom centered Gaussian orbitals. High quality all-electron basis sets used in previous studies [18–20] were adopted to describe the Cu and O ions and the outermost exponents re-optimized *in situ*. This resulted in the use of a quadruple valence set for the Cu-ion of structure 864111-D31 with outer sp exponents (in a_0^{-2}) of 1.582, 0.559 and 0.15 and outer d-exponent of 0.430. The triple valence O basis set, 8411D, had outer sp-exponents of 0.425 and 0.125 with a d-exponent of 0.5. The Sr ion was described using a core pseudopotential and double valence basis set [21]. The Coulomb and exchange series were truncated using overlap criteria documented elsewhere [16] (strict tolerances of 777714 were adopted) and the exchange correlation potentials and energy were integrated numerically on an atom centered grid of points containing approximated 2500 symmetry irreducible points per atom (the XLGRID option [16]). Finally k-space integration was performed on a Pack-Monkhurst grid defined by a shrinking factor of eight which contained 59 symmetry irreducible points.

K-doped SrCu_2O_2 was prepared as described previously [22]. Phase purity was established by X-ray powder diffraction. K-doping pins the Fermi level close to the valence band edge and prevents potential problems due to sample charging during the photoemission experiments. However the doping does not significantly alter the overall appearance of the main valence band photoemission spectra [22].

Optimisation of cleaning procedures and initial surface characterisation was carried out in a Scienta ESCA 300

spectrometer operated under the aegis of the National Centre for Electron Spectroscopy and Surface Analysis (NCESS) at Daresbury Laboratory (UK). This incorporates a rotating anode Al $K\alpha$ X-ray source, a seven crystal X-ray monochromator and a 300 mm mean radius spherical sector electron energy analyser with channel plate electron detection system. The effective instrument resolution was 350 meV. Photoemission spectra of as-presented samples of pure or K-doped SrCu_2O_2 showed strong C 1s core lines due to both hydrocarbon and carbonate contamination. In addition the Cu 2p core lines showed very strong satellites characteristic of CuO. Finally the K 2p/Sr 3p intensity ratio was a factor of 10 higher than expected from the nominal doping level, indicating pronounced K surface segregation, probably in the form of K_2CO_3 . After UHV annealing at 700 °C or above the CuO 2p satellite peaks were suppressed. Additionally the C 1s impurity structure was almost eliminated and the K 2p/Sr 3p intensity ratio was restored to a value tolerably close to that expected from the nominal composition: after correction with atomic sensitivity factors [23], the K 2p and Sr 3p peak intensities for 2.5%-doped SrCu_2O_2 gave a K/Sr atomic ratio of 0.035. Further removal of carbon was achieved by argon ion bombardment and annealing at temperatures up to 800 °C.

Vacuum UV photoemission spectra were measured on beamline 4.1 of the synchrotron radiation source at Daresbury Laboratory UK. The beamline incorporates a monochromator with three spherical gratings covering the photon energy ranges 14–60 eV, 50–140 eV and 100–170 eV. The nominal monochromator resolution was 40 meV at $h\nu = 50 \text{ eV}$, increasing to 120 meV at $h\nu = 150 \text{ eV}$. The spectrometer was housed in a turbomolecular pumped single chamber UHV system with a base pressure of 2×10^{-10} mbar. The chamber was equipped with a Scienta SES200 hemispherical electron energy analyser with a mean radius of 200 mm and angular acceptance of $\sim 10^\circ$. The pass energy was set at 40 eV in all experiments, giving a nominal analyser resolution of 80 meV.

A pellet sample of 2% K-doped SrCu_2O_2 was secured to a tantalum backing plate on the sample manipulator with tantalum wire. Following the recipe used in the XPS system, the pellet was cleaned by first annealing at progressively higher temperatures of 455 °C, 660 °C and 730 °C for 1 h each, followed by argon ion bombardment with 1.5 keV ions at a current of 10–12 μA . This was followed by further annealing in UHV first at 730 °C for 1 h and then 800 °C for 1 h. After the higher temperature anneal there was obviously near complete compensation of hole charge carriers by oxygen vacancies and the sample gave indication of pronounced sample charging. Conductivity was restored by a final anneal in 6×10^{-7} mbar O_2 at 500 °C for 1 h. Spectra before and after the highest temperature anneal and subsequent oxygen treatment were little different.

The full and partial densities of states derived from the bandstructure calculations are shown in Fig. 1. The band-gap is found to be direct with value of 3.4 eV, very close to

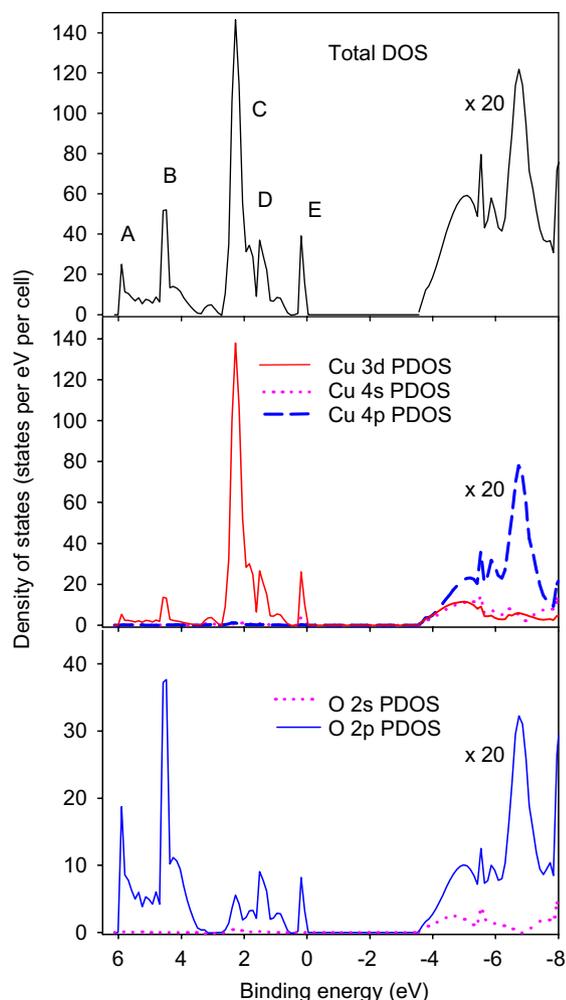


Fig. 1. Full and partial densities of states for SrCu_2O_2 . Note the different vertical scale for the lowest panel.

the experimental value of 3.3 eV. The valence band has an overall width of about 6 eV and contains five main features labelled A–E in Fig. 1. Inspection of the partial densities of states reveals that A and B are of dominant O 2p character whilst C, D and E are of dominant Cu 3d character. However there is significant mixing between O 2p states and Cu 3d states, particularly at the top and bottom of the valence band. Thus the states at the peak maximum in band A have 78% O 2p character and 22% Cu 3d character, whilst in band B the analogous figures are 74% O 2p and 26% Cu 3d. Correspondingly, the states in band E have 76% Cu 3d character but also about 24% O 2p character. By contrast the most tightly bound Cu 3d states in band C are of almost pure (96%) Cu 3d character with only 4% O 2p admixture. These findings are in accord with the qualitative ideas developed above which suggest that the local linear coordination of Cu should inhibit mixing between O 2p and Cu $3d_{xy}$ and $3d_{x^2-y^2}$ states. The conduction band SrCu_2O_2 is of dominant Cu 4p and Cu 4s character, but owing to covalency there is also a substantial contribution from O 2p and Cu 3d states.

Vacuum UV photoemission spectra excited over a range of photon energies between 38 eV and 154 eV are shown in Fig. 2. The intensity of the displayed spectra has been scaled with reference to the output from a copper drain mesh photon flux monitor and further corrected to allow for the variation in quantum efficiency of the monitor itself. Fig. 3 shows a single spectrum excited at 110 eV in further detail. The spectra may be fitted to five components labelled A–E in the figure. The variation in intensity with photon energy of these five components is shown in Fig. 4. The three bands at lower binding energy show an overall increase in intensity with increasing photon energy, but with a distinct anti-resonance minimum around 75 eV photon energy. This corresponds to the threshold for ionisation of Cu 3p core states. Similar behaviour has been observed before for Cu_2O ²⁴ and attributed to interference between the direct ionisation channel:

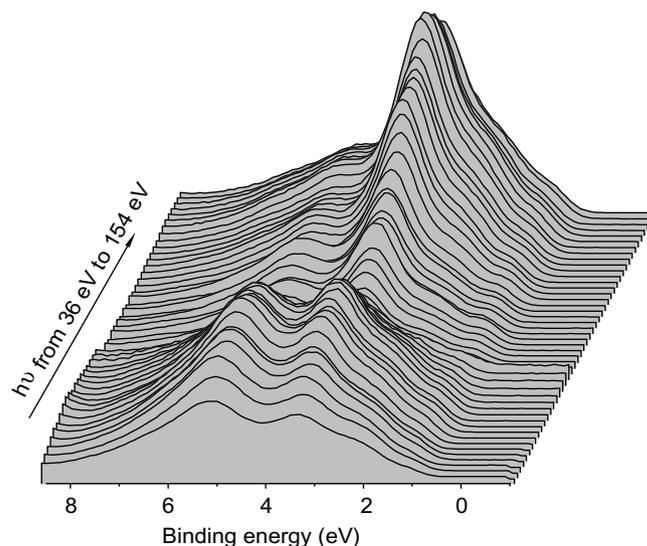
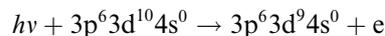


Fig. 2. Valence band photoemission spectra of K-doped SrCu_2O_2 excited over a range of photon energies between 38 eV and 158 eV.

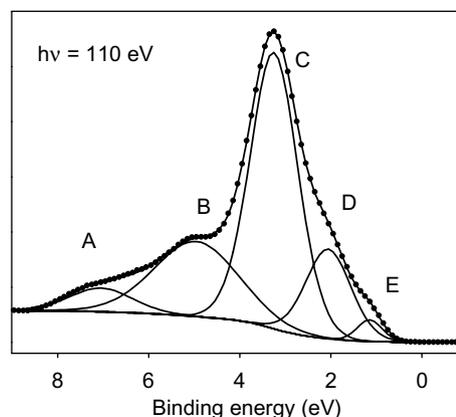


Fig. 3. Typical curve fit to photoemission spectrum of K-doped SrCu_2O_2 excited at 110 eV photon energy.

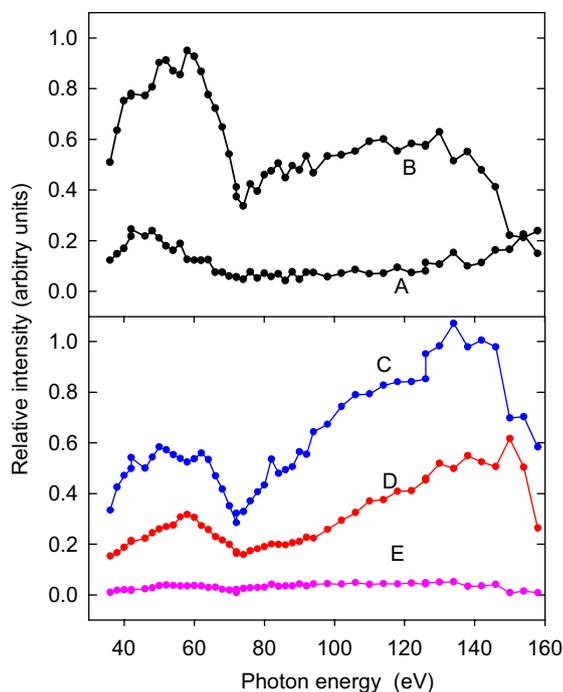
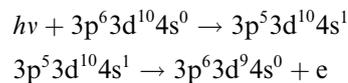


Fig. 4. Variation in intensity with photon energy of the five components to valence band photoemission spectra of K-doped SrCu_2O_2 derived from curve fits as in Fig. 2.

and a resonant excitation channel that is followed by Auger decay:



The observed intensity variations therefore establish that the states corresponding to bands C, D and E are of dominant Cu 3d atomic character. By contrast bands A and B show an overall decrease in intensity with increasing photon energy. This is as to be expected for states of dominant O 2p atomic character because over the photon energy range we have investigated there is decrease in the O 2p cross-section. However there is still evidence of anti-resonance behaviour around the Cu 3p core threshold in bands A and B. This shows that the electronic states in the lower part of the valence band have some Cu 3d atomic character.

In principle intensity changes in photoemission spectra as a function of photon energy can be used to quantify the atomic make up of hybridised states. However owing to the strong anti-resonance effect in the Cu 3d states, we cannot simply use computed one electron cross-sections. We have therefore attempted to fit the experimental cross-section profile shown for band B using the empirical curve for band C to represent the change in relative cross-section for Cu 3d states along with the one electron cross-section for O 2p states derived from the tabulations of Yeh and Lindau [23]. It was further necessary to put the Cu 3d cross section profile onto an absolute rather than relative footing. This was achieved using the absolute absorption

cross-section for photoabsorption in Cu vapour [25] below the Cu 3p resonance. In this way we estimate that the states in band B have $20 \pm 5\%$ Cu 3d character. This is in reasonable agreement with the value of 26% derived from the calculations. The qualitative conclusion that there is significant mixing of Cu 3d states into O 2p states is in accord with previous high resolution XPS measurements where the overall valence band spectrum is dominated by the Cu 3d partial density of states [22].

Photoemission spectra accumulated over an extended range to include shallow core level and satellite structure are shown in Fig. 5. Aside from the Sr 4p and K 3p shallow core lines, two satellites are observed centred at binding energies of 15.5 eV and 10.0 eV, respectively. These are labelled s1 and s2 in Fig. 5. Both show resonant enhancement around the core threshold, with maximum intensities at about 78 eV and 70 eV, respectively. These satellites are similar to those found in Cu_2O and CuO [24], respectively and correspond to Cu $3d^8$ final states. Observation of the s2 satellite provides evidence for the existence of Cu^{2+} hole states in the near surface region probed in UV photoemission.

In summary we have studied UV photoemission spectra of K-doped SrCu_2O_2 over a range of photon energies between 38 eV and 164 eV. The photoemission spectra are in excellent agreement with partial densities of states derived from calculations using hybrid exchange density functional theory and provide a direct quantitative measurement of the pronounced hybridisation between Cu 3d and O 2p states in the valence band. We plan further work to establish the nature of the charge carriers in more detail. In particular cluster calculations or large super-cell calculations are needed to establish the extent of relaxation of

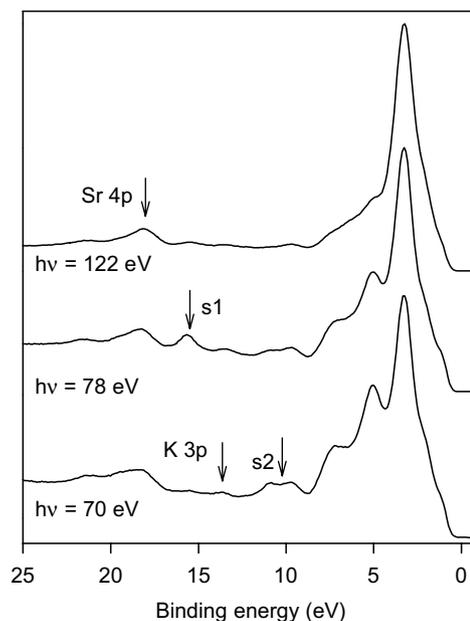


Fig. 5. Photoemission spectra of K-doped SrCu_2O_2 excited at the three photon energies indicated. The spectral range is extended to show Cu satellite structure and the shallow core Sr 4p level.

oxygen ions around the hole carriers, whilst electron paramagnetic resonance experiments on ^{17}O enriched samples will be used to provide a measure of the extent of hole delocalisation onto oxygen. The present results confirm the ability [18,26] of hybrid Hamiltonian techniques to calculate realistic absolute values of fundamental band gaps in complex oxides.

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