Understanding conductivity in SrCu_2O_2 : stability, geometry and electronic structure of intrinsic defects from first principles†

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Density functional theory calculations have been performed on stoichiometric and intrinsically defective p-type transparent conducting oxide SrCu_2O_2 , using GGA corrected for on-site Coulombic interactions (GGA + U). Analysis of the absorption spectrum of SrCu_2O_2 indicates that the fundamental direct band gap could be as much as ~ 0.5 eV smaller than the optical band gap. Our results indicate that the defects that cause p-type conductivity are favoured under all conditions, with defects that cause n-type conductivity having significantly higher formation energies. We show conclusively that the most stable defects are copper and strontium vacancies. Copper vacancies introduce a distinct acceptor single particle level above the valence band maximum, consistent with the experimentally known activated hopping mechanism.

I. Introduction

In recent years, transparent conducting oxides (TCOs) have been extensively studied due to their utility in optoelectronic devices such as solar panels, heatable glass, touch panels and flat panel displays.^{1–3} However, in order to develop the field further and move into the area of “transparent electronics” it is essential to develop both p- and n-type TCO materials. n-type TCOs such as SnO_2 ,⁴ In_2O_3 ⁵ and ZnO ⁶ have been produced with conductivities as high as $\sim 10^4$ S cm^{-1} . p-type TCOs, however, have proved quite difficult to develop, and the few that do exist display conductivities that remain quite low, with the highest conductivity achieved in Mg-doped CuCrO_2 at 220 S cm^{-1} .⁷ It is thus of great importance to investigate the origins behind p-type conductivity in these materials so that new improved TCOs can be designed.

In order to remain transparent, TCOs must have an optical band gap greater than 3.1 eV,³ which is large enough to allow visible light photons to pass through the material without exciting electrons from the valence band to the conduction band. However, materials with such a wide band gap normally behave as insulators in their stoichiometric form and conductivity can only occur through the presence of intrinsic defects or extrinsic dopants. These can produce p-type conductivity through the introduction of excess holes to the system or n-type conduction through the presence of excess electrons.

p-type TCOs have proved more difficult to produce than n-type due to the valence band (VB) composition of most wide band gap metal oxides. The top of the VB in most n-type TCOs is dominated by oxygen 2p states. Holes introduced into this type of system are strongly localised on the oxygen atoms, and result in acceptor levels that are deep in the band gap with a large energy barrier of migration resulting in poor conductivity.^{8,9}

Hosono *et al.*^{10,11} have overcome this problem using the method of “chemical modulation of the valence band”. By choosing a suitable cation, the valence band can be modified through the hybridisation of cation d and oxygen p orbitals. This encourages the holes to delocalise, resulting in shallower, less localised acceptor levels above the valence band which make p-type conductivity possible. The archetypal p-type material is Cu_2O , in which the valence band is made up of hybridised Cu 3d and O 2p states. The introduction of defects such as copper vacancies and oxygen interstitials leads to less localised holes, with acceptor levels above the valence band maximum.^{12–14} However, the band gap of Cu_2O (~ 2.17 eV¹⁵) is too small for transparency preventing its use as a TCO. This problem has been overcome through alloying Cu_2O with Al_2O_3 to produce one of the first known p-type TCOs, CuAlO_2 ¹⁰ which has an optical band gap of 3.5 eV, and preserves the p-type conducting properties of the Cu_2O structure. Following this, many other p-type TCOs have been developed such as CuGaO_2 ,¹⁶ CuInO_2 ,¹⁷ CuCrO_2 ,¹⁸ CuBO_2 ¹⁹ and SrCu_2O_2 .²⁰

For the production of p–n junctions, a TCO with a direct band gap is preferable.²¹ Unfortunately, most known p-type TCOs (e.g. CuCrO_2 , CuAlO_2 ¹⁸) have indirect band gaps. SrCu_2O_2 is the only known p-type TCO with a direct band gap (3.3 eV at T^{20}) and has hence attracted much attention in recent years. A successful p–n junction of p-type SrCu_2O_2 in combination with n-type ZnO has already been fabricated.^{22,23}

SrCu_2O_2 crystallises in a tetragonal structure in space group $I41/amd$ with a unit cell defined by the lattice constants $a = 5.480$ Å and $c = 9.825$ Å²⁴ as shown in Fig. 1. Each Cu atom coordinates linearly to two oxygen atoms to form zigzag chains of O–Cu–O bonds in the orthogonal [100] and [010] directions. Each Sr ion is surrounded by a distorted octahedron of oxygen atoms which lie linearly along the c -axis giving a compressed SrO_6 octahedron.

Conductivity in undoped SrCu_2O_2 arises from the presence of holes which are introduced by oxygen-excess which is presumed to be due to the presence of intrinsic defects such as Cu vacancies

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Fig. 1 Unit cell of SrCu_2O_2 . Green atoms are Sr, yellow are Cu and red are O.

or oxygen interstitials. Conductivity in SrCu_2O_2 is known to occur *via* a thermally activated mechanism with activation energy of 0.2 eV.^{20,25} Conduction is thought to occur through small-polaron hopping similar to that found for the copper delafossite TCOs.²⁶ So far the conductivity of undoped SrCu_2O_2 remains quite low at $5.3 \times 10^{-2} \text{ S cm}^{-1}$.²⁷ It is possible to improve the conductivity through the introduction of dopants such as K^{25,28,29} which improves conductivity through increased hole concentration or Ca^{30,31} which has been reported to improve conductivity by lowering the hole effective mass whilst increasing the band gap to give better transparency. However, the exact defects and mechanism responsible for p-type conductivity in the undoped system are not well understood.

Although some computational work on SrCu_2O_2 has been performed, it has tended to be focused on the electronic structure of the pure material without analysis of the defect structure.^{28,30–35} Electronic structure calculations have shown a direct gap at Γ with the valence band being composed of a mixture of Cu 3d and O 2p states.^{28,31–33,35,36} Comparison with experimental X-ray photoelectron spectroscopy (XPS) shows density functional theory (DFT) calculations to accurately reproduce the valence band features of SrCu_2O_2 when compared to experimental photoemission spectra.²⁸

To the best of our knowledge there is only one previous computational study on intrinsic defects in SrCu_2O_2 which was carried out using GGA-DFT.³⁷ The only defects considered were copper and oxygen vacancies, with no consideration of any other possible intrinsic defects which may occur in the system and no consideration of the electronic structure of any defects. As conductivity in SrCu_2O_2 is thought to occur *via* a polaronic hole-hopping mechanism,²⁵ the defect structure should be polaronic in nature. However, GGA/LDA DFT is well-known to have problems in localising defects due to the self-interaction error,

and thus it is unlikely to result in even a qualitatively correct defect structure.

We have performed a detailed study of the electronic structure of SrCu_2O_2 and its intrinsic defects using the GGA + U methodology to correct for some of the inadequacies of standard GGA/LDA treatments. Our study (i) reveals the difference between the fundamental band gap and the optical band gap, which is as much as $\sim 0.5 \text{ eV}$, (ii) examines the various possible defects which may cause oxygen-excess and hence p-type conductivity as well as considering defects which would induce oxygen deficiency and n-type conductivity, (iii) demonstrates that the defects which cause p-type conductivity are energetically accessible under all conditions, (iv) shows that strontium and copper vacancies are the lowest energy defects and (v) shows copper vacancies to produce distinct single particle levels above the valence band maximum consistent with a small-polaron hopping mechanism of conduction.

II. Computational methods

All calculations were carried out using periodic density functional theory (DFT) as implemented in the VASP code.³⁸ The wave functions were represented using a plane wave basis set with the projected augmented wave method³⁹ used to represent the interaction between the core (Cu: [Ar], Sr: [Ni], O: [He]) and valence electrons. Exchange and correlation were treated using the Perdew–Burke–Ernzerhof⁴⁰ gradient correlated functional, with corrections for the on-site Coulomb interactions for strongly correlated systems (GGA + U).⁴¹ Uncorrected GGA calculations have been shown to be unsuitable for describing systems with localised electronic defects.⁴² Fig. 2 shows the band structure for a Cu vacancy defect as calculated using uncorrected

Fig. 2 The band structure of a Cu vacancy in SrCu_2O_2 as calculated using uncorrected GGA calculations (a) shows the α -spin bands and (b) shows the β -spin bands. The dashed line indicates the highest occupied level.

GGA, which shows the absence of any distinct single particle level in the band gap. Indeed, GGA predicts a formally metallic system for the Cu vacancy, with the single particle level clearly crossing the Fermi level. This is completely at variance with the known activated conduction mechanism in this material,^{20,25} and further highlights the unsuitability of LDA/GGA in describing materials with polaronic conduction.²⁵ GGA + *U* calculations have previously been shown to result in the correct localisation behaviour for both n-type^{43–47} and p-type^{48,49} defects. The value of *U* employed in the GGA + *U* calculations was 5.2 eV, which has been shown to accurately reproduce the valence band photoemission spectra of CuAlO₂ and CuCrO₂.^{18,50} The use of a +*U* correction on Cu(I) based materials is discussed elsewhere.⁵¹ The calculations were fully spin polarised in order to properly describe the unpaired electrons produced upon defect formation.

The equilibrium lattice parameters were calculated by performing structural optimisations on bulk SrCu₂O₂ at a series of volumes, allowing the atomic positions, lattice vectors, and the cell angles to relax while the total volume was held constant. The resulting energy–volume curves were fitted to the Murnaghan equation of state⁵² to obtain the equilibrium bulk cell volume. A 4 × 4 × 2 Monkhorst–Pack⁵³ *k*-point grid was used for the unit cell with a plane wave energy cutoff of 500 eV. Defect calculations were performed in a 2 × 2 × 1 supercell containing 80 atoms with a 2 × 2 × 2 Monkhorst–Pack *k*-point grid. The structural optimisations were deemed to be converged when the force on every ion was less than 0.01 eV Å^{−1}.

The following equation was used in order to calculate defect formation energies:

$$E_f(D) = E_{\text{tot}}(D) - E_{\text{tot}}(\text{SrCu}_2\text{O}_2) + n_{\text{Sr}}E(\text{Sr}) + n_{\text{Cu}}E(\text{Cu}) + \frac{1}{2}n_{\text{O}}E(\text{O}_2) + n_{\text{Sr}}\mu_{\text{Sr}} + n_{\text{O}}\mu_{\text{O}} + n_{\text{Cu}}\mu_{\text{Cu}} \quad (1)$$

where $E_{\text{tot}}(D)$ and $E_{\text{tot}}(\text{SrCu}_2\text{O}_2)$ are the total energies of the defective and pure supercells; $E(\text{Sr})$, $E(\text{Cu})$ and $E(\text{O}_2)$ are the energies of an Sr atom in Sr metal, Cu atom in Cu metal and an O₂ molecule respectively; n_A is the number of atoms of A exchanged with the external atomic reservoir and μ_A is the chemical potential of element A.

Varying the chemical potentials relates to varying the partial pressures experimentally. They can thus be used to set the different conditions under which SrCu₂O₂ may form, and determine the optimum conditions for defect formation. The chemical potentials are limited to a range determined by the formation enthalpy of SrCu₂O₂ at 0 K in order to maintain a stable compound:

$$\mu_{\text{Sr}} + 2\mu_{\text{Cu}} + 2\mu_{\text{O}} = \Delta H_f(\text{SrCu}_2\text{O}_2) \quad (2)$$

We calculated ΔH_f for SrCu₂O₂ to be −7.27 eV compared to its experimentally determined value of −8.21 eV.⁵⁴ This is quite a large error, however, it is uncertain how reliable the experimental data are as there is very little thermodynamic data available in the literature for SrCu₂O₂. In addition theoretical data have long been known to have significant errors with respect to the experimental formation energies.⁵⁵ To avoid precipitation into solid elemental Sr, Cu and O₂ gas we also require:

$$\mu_{\text{Sr}} \leq 0, \mu_{\text{Cu}} \leq 0, \mu_{\text{O}} \leq 0 \quad (3)$$

The chemical potentials are further constrained by the decomposition of SrCu₂O₂ into binary compounds. The atomic chemical potentials thus must obey the inequalities:

$$\mu_{\text{Cu}} + \mu_{\text{O}} \leq \Delta H_f(\text{CuO}) \quad (4)$$

$$2\mu_{\text{Cu}} + \mu_{\text{O}} \leq \Delta H_f(\text{Cu}_2\text{O}) \quad (5)$$

$$\mu_{\text{Sr}} + \mu_{\text{O}} \leq \Delta H_f(\text{SrO}) \quad (6)$$

The calculated formation enthalpies for CuO, Cu₂O and SrO are −1.36, −1.55 and −5.50 eV compared to experimentally determined values of −1.63,⁵⁶ −1.75⁵⁶ and −6.14 eV⁵⁷ respectively. Through the linear combination of eqn (4)–(6) with eqn (2) the boundaries between SrCu₂O₂ and the binary compounds can be defined. For example combining eqn (4) with eqn (2) gives the inequality:

$$\mu_{\text{Sr}} \geq \Delta H_f(\text{SrCu}_2\text{O}_2) - 2\Delta H_f(\text{CuO}) \quad (7)$$

which results in the limit $\mu_{\text{Sr}} \geq -4.54$ eV to avoid decomposition to CuO. Similarly, the Cu₂O limit can be derived as $\mu_{\text{Sr}} - 2\mu_{\text{Cu}} \geq -4.17$ eV and that for SrO formation is defined as $\mu_{\text{Sr}} - 2\mu_{\text{Cu}} \leq -3.73$ eV. Using these limits and the approach of Walsh *et al.*⁵⁸ and Persson *et al.*,⁵⁹ the phase diagram for SrCu₂O₂ can be drawn up as in Fig. 3 which shows the range of chemical potentials under which SrCu₂O₂ forms.

The triangle vertices correspond to Sr/O-rich conditions ($\mu_{\text{Sr}} = \mu_{\text{O}} = 0.00$ eV, $\mu_{\text{Cu}} = -3.63$ eV), Cu/O-rich conditions ($\mu_{\text{Sr}} = -7.27$ eV, $\mu_{\text{Cu}} = \mu_{\text{O}} = 0.00$ eV) and Cu/Sr-rich conditions ($\mu_{\text{Sr}} = \mu_{\text{Cu}} = 0.00$ eV, $\mu_{\text{O}} = -3.63$ eV) and are calculated directly from eqn (2). The boundaries for binary

Fig. 3 The phase diagram of SrCu₂O₂ indicating the range of chemical potentials (in eV) under which SrCu₂O₂ is stable. (a) Calculated phase triangle using formation energies from GGA + *U* calculations. (b) Phase diagram found using experimental formation energies.^{56,57}

phase formation result in a narrow range of chemical potentials under which SrCu_2O_2 is thermodynamically stable. Our results show good agreement with the stability region found by repeating the above methodology using the experimental formation enthalpies (experimental values taken from ref. 56 and 57) in Fig. 3b. This explains the narrow range of oxygen partial pressures under which SrCu_2O_2 forms experimentally.⁶⁰

The four sets of chemical potentials marking the boundaries of stability are marked A, B, C and D in Fig. 3. The region under which SrCu_2O_2 forms corresponds to relatively copper-rich, strontium-poor and oxygen-poor conditions. We have calculated defect energies using these four sets of conditions in order to examine the differences in the defect equilibrium which result. Condition A corresponds to $\mu_{\text{Sr}} = -4.16$ eV, $\mu_{\text{Cu}} = 0.00$ eV, and $\mu_{\text{O}} = -1.55$ eV which is at the copper-rich limit of the stability region combined with a mid-range Sr chemical potential with μ_{O} being relatively low. Condition B ($\mu_{\text{Sr}} = -3.72$ eV, $\mu_{\text{Cu}} = 0.00$ eV, $\mu_{\text{O}} = -1.77$ eV) is at the Sr-rich, O-poor, Cu-rich limits of the stability region and should therefore favour the formation of the oxygen-poor defects—Sr interstitials, O vacancies and Cu interstitials. Condition C ($\mu_{\text{Sr}} = -4.54$ eV, $\mu_{\text{Cu}} = -0.41$ eV, $\mu_{\text{O}} = -0.95$ eV) corresponds to Sr-poor, Cu-poor and O-rich limits of the stability region and should favour oxygen-excess defects—Sr/Cu vacancies and O interstitials. Finally condition D ($\mu_{\text{Sr}} = -4.54$ eV, $\mu_{\text{Cu}} = -0.19$ eV, $\mu_{\text{O}} = -1.17$ eV) is at the Sr-poor limit with μ_{Cu} and μ_{O} having mid-range values.

III. Bulk electronic structure

The optimised cell parameters and bond lengths are shown in Table 1. The calculated lattice vectors and bond lengths for SrCu_2O_2 show good agreement with experiment,²⁴ showing a slight overestimation as expected for GGA + *U* calculations. The *a* lattice vector is overestimated by 0.4% while the *c* vector is overestimated by 0.5% compared to experimental values. Each Cu ion is coordinated linearly to two O ions with a calculated bond distance of 1.85 Å while each Sr ion is coordinated linearly between two oxygen ions with a bond distance of 2.47 Å.

The calculated band structure for SrCu_2O_2 is shown in Fig. 4. The eigenvalues for the structure were plotted along the high symmetry directions as defined by Bradley and Cracknell.⁶¹ The valence band maximum (VBM) and conduction band minimum (CBM) both occur at Γ making SrCu_2O_2 a direct gap material with a calculated band gap of 2.1 eV. The band gap is underestimated compared to its experimental optical value of 3.3 eV²⁰ due to the well-known GGA error. The VBM shows a small dispersion at Γ while the CBM shows a larger dispersion.

In order to estimate carrier mobility in SrCu_2O_2 we have calculated the effective masses at the VBM and CBM. The VBM effective mass gives insight into p-type conductivity while the

Table 1 Calculated lattice parameters and bond lengths for SrCu_2O_2 compared to their experimental values²⁴

	Calculated (error)	Experimental
<i>a</i> /Å	5.50 (+0.4%)	5.48
<i>c</i> /Å	9.87 (+0.5%)	9.83
Cu–O/Å	1.85 (+0.4%)	1.84
Sr–O/Å	2.47 (+0.5%)	2.46

Fig. 4 Band structure of pure SrCu_2O_2 plotted along the high symmetry directions. The dashed line indicates highest occupied level.

CBM effective mass gives an estimate of the electron mobility for n-type conductivity. The effective masses for the VBM and CBM of SrCu_2O_2 were calculated according to the equation:

$$\frac{1}{m^*(E)} = \frac{1}{\hbar^2 k} \frac{dE}{dk} \quad (8)$$

where $E(k)$ is the band-edge energy as a function of the wave vector k which is obtained directly from the GGA + *U* calculations. This assumes that the first derivative of $E(k)$ is the same as that of a parabolic band at the same k -point. As the VBM of SrCu_2O_2 is not perfectly parabolic and conduction in this case is thought to occur through a polaronic-hopping mechanism^{20,25} rather than a band conduction mechanism, the calculated masses can only serve as an approximate indication of conductivity.

Table 2 shows the calculated effective masses along the high symmetry directions in SrCu_2O_2 . The lowest VBM effective mass was found in the direction Γ –N and has a value of 0.79 m_0 while the lowest CBM effective mass was along Γ –X with a magnitude of 0.49 m_0 . This demonstrates SrCu_2O_2 to have better electron mobility for n-type conductivity than hole mobility for p-type conductivity. This may be one of the reasons why it demonstrates such low p-type conductivities experimentally.

The calculated total electronic density of states (EDOS) and the partial electronic density of states (PEDOS) for SrCu_2O_2 are shown in Fig. 5. The atomic projections were calculated using sphere radii of 1.55 Å for Sr, 1.45 Å for Cu and 1.45 Å for O. These values were determined by considering the calculated valence electron density around each ion and electron counting. Examining the density of states in Fig. 5 shows the valence band to have three distinct regions marked I, II and III. In region I, the lower valence band between -5.3 and -2.8 eV, states of O 2p character hybridise with states of Cu 3d character, with the Cu 3d states dominating. Between -2.8 and -2 eV (region II) states of Cu 3d character dominate with very little contribution from O 2p states. Finally in region III, the upper part of the valence band from -2 eV to the VBM, there is significant hybridisation of O 2p and Cu 3d states, with the Cu 3d dominating. Sr ions provide

Table 2 Calculated effective masses (in m_0) at the VBM and CBM of SrCu_2O_2 along the high symmetry directions

	Γ –Z	Γ –N	Γ –X
VBM	2.87	0.79	1.54
CBM	1.24	1.65	0.49

Fig. 5 Total and partial electronic density of states (EDOS/PEDOS) of SrCu_2O_2 . Blue lines indicate s states, red are p states and green are d states. The dashed line indicates the highest occupied state (the VBM).

very little contribution to the valence band. The covalency in bonding is also reflected by examination of the Bader charges.⁶² These show the Sr ions to have a charge of +1.55, the Cu to have a charge of 0.45 and the O to have a charge of -1.23 compared to the charges expected in a fully ionic model of +2, +1 and -2 respectively.

IV. Optical versus fundamental band gap

It has been demonstrated recently that the fundamental direct band gaps in both n-type and p-type TCOs do not always correspond to the optical band gaps as measured experimentally.^{5,63} In the case of Cu-based delafossites, Nie *et al.* have shown that the lowest direct VB–CB transition in CuMO_2 ($M = \text{Al, Ga, In}$) is not symmetry allowed, and thus have explained the apparent band gap anomalies seen in group 13 delafossites.⁶³ A difference of 0.8 eV has been noted between the fundamental direct band gap and the optical band gap in In_2O_3 .⁵ Similar symmetry forbidden direct fundamental gaps have also been noted in other conducting oxide structures including cuprite Cu_2O ,⁶⁴ rutile SnO_2 , TiO_2 and GeO_2 ,^{65,66} and spinel SnZn_2O_4 , SnCd_2O_4 and CdIn_2O_4 .⁶⁷ A previous theoretical study of SrCu_2O_2 reported that the direct dipole transition from the VBM to the CBM is also forbidden,³¹ but the authors have not attempted to quantify the effect (if any) this will have on the fundamental versus optical band gap measurements.

We have calculated optical transition matrix elements and the optical absorption spectrum of SrCu_2O_2 within the transversal approximation and PAW method as implemented in the VASP code.⁶⁸ In this methodology, the absorption spectra are summed over all direct VB to CB transitions and therefore ignores indirect and intraband absorptions.⁶⁹ Within this framework of single particle transitions, the electron–hole correlations are not treated, and so would require treatment by higher order electronic structure methods.^{70,71} Nevertheless, this method has been previously shown to provide reasonable optical absorption spectra.^{63,72,73}

Fig. 6 Calculated optical absorption spectrum of SrCu_2O_2 summed over all possible direct valence to conduction band transitions. The magnitude of the fundamental direct band gap is shown by the dashed blue line; the onset of optical absorption is denoted by a dashed red line.

The optical absorption spectrum for SrCu_2O_2 is shown in Fig. 6. For SrCu_2O_2 , we find that the fundamental band-edge transitions at the Γ point are symmetry disallowed, consistent with the work of Nie *et al.*³¹ Optical absorption begins at ~ 2.6 eV, compared to our calculated fundamental direct band gap of ~ 2.1 eV. Analysis of the calculated optical transition matrix tells us that the lowest energy allowed optical transition is from the VBM to the second conduction band at Γ . This corresponds to a difference of ~ 0.5 eV between the optical and fundamental band gaps of this material.

V. Intrinsic defects

There are a number of intrinsic defects which can occur in SrCu_2O_2 . p-type conductivity may be caused by the formation of oxygen-excess defects such as Cu(I) vacancies (V_{Cu}'), O^{2-} interstitials (O_i'') or Sr(II) vacancies (V_{Sr}''), which lead to conductivity through charge-compensating holes ($h^\cdot$). Alternatively, if oxygen-deficient defects such as O^{2-} vacancies ($V_{\text{O}}^\cdot$), Cu(I) interstitials (Cu_i) or Sr(II) interstitials (Sr_i) form, the result would be n-type conductivity through charge-compensating electrons (e'). To achieve good p-type conductivity in SrCu_2O_2 , we thus require the defects which cause p-type conductivity to have low formation energies, while those causing n-type conductivity should have higher formation energies to avoid the recombination of electrons and holes and subsequent loss in conductivity.

In this section we have first calculated the formation energies and identified the most stable defects. We discuss the positions of the single particle levels in the band gap for each defect and finally we give a detailed discussion of the electronic structures of the most stable defects $-V_{\text{Cu}}' + h^\cdot$ and $V_{\text{Sr}}'' + 2h^\cdot$.

A. Defect formation energies

Table 3 shows the formation energies of defects in SrCu_2O_2 without taking chemical potentials into account. The defects have been split into two groups—those causing oxygen deficiency and those causing oxygen-excess. As SrCu_2O_2 is known to become non-stoichiometric through oxygen-excess, it could be expected that the defects causing oxygen-excess would be much lower in energy while oxygen-deficient defects should be energetically unfavourable.

Table 3 Defect formation energies (in eV) in SrCu₂O₂ without taking chemical potential into account. Split $V_{\text{Cu}}' + h' = 2V_{\text{Cu}}' + \text{Cu}_i$

Defects	Energy/eV
Oxygen-excess	
$V_{\text{Cu}}' + h'$	1.29
Split $V_{\text{Cu}}' + h'$	2.12
$\text{O}_i'' + 2h'$	0.68
$V_{\text{Sr}}'' + 2h'$	5.50
Oxygen-deficient	
$V_{\text{O}}' + 2e'$	4.06
$\text{Sr}_i' + 2e'$	0.85
$\text{Cu}_i + e'$	2.54

The defect with the lowest energy overall is $\text{O}_i'' + 2h'$ with a formation energy of 0.68 eV suggesting oxygen-excess in SrCu₂O₂ to be caused by oxygen interstitials. $\text{Sr}_i' + 2e'$ is the lowest energy defect for oxygen deficiency with a formation energy of 0.85 eV. Conversely, $V_{\text{Sr}}'' + 2h'$ has a very high formation energy suggesting that it would be unlikely to be the major cause of oxygen-excess in the material, while $V_{\text{O}}' + 2e'$ is unlikely to form as charge-killer defect due to its high formation energy.

However, the inclusion of chemical potentials leads to a complete alteration of the trends in Table 3, due to the restricted chemical potential range under which SrCu₂O₂ forms. This is shown in Table 4 under the four conditions marked in Fig. 3. As the area in the phase diagram under which SrCu₂O₂ is stable corresponds to Sr-poor conditions with the oxygen chemical potential also being relatively low, oxygen and strontium interstitials are destabilised under all conditions while Sr vacancies become more stable. The formation energies of copper defects are less affected by the change in chemical potential as in the SrCu₂O₂ stability region, the copper chemical potential is close to zero giving copper-rich conditions.

Under condition A corresponding to copper-rich conditions ($\mu_{\text{Cu}} = 0$ eV) with the strontium and oxygen chemical potentials having mid-range values ($\mu_{\text{Sr}} = -4.16$ eV, $\mu_{\text{O}} = -1.55$ eV), the lowest energy defect is $V_{\text{Cu}}' + h'$. $V_{\text{Sr}}'' + 2h'$ also has a low formation energy of 1.34 eV and may also contribute to the overall defect structure. $\text{Sr}_i' + 2e'$ is very high in energy and is unlikely to form and all of the oxygen-deficient defects are higher in energy than oxygen-excess defects. Hence these conditions will result in a net non-stoichiometry due to oxygen-excess.

Condition B corresponds to copper-rich conditions ($\mu_{\text{Cu}} = 0$ eV) with the strontium chemical potential having its highest

Table 4 Defect formation energies (in eV) in SrCu₂O₂ under the four chemical potential limits of stability. Split $V_{\text{Cu}}' + h' = 2V_{\text{Cu}}' + \text{Cu}_i$ A: $\mu_{\text{Sr}} = -4.16$ eV, $\mu_{\text{Cu}} = 0.00$ eV, $\mu_{\text{O}} = -1.55$ eV; B: $\mu_{\text{Sr}} = -3.72$ eV, $\mu_{\text{Cu}} = 0.00$ eV, $\mu_{\text{O}} = -1.77$ eV; C: $\mu_{\text{Sr}} = -4.54$ eV, $\mu_{\text{Cu}} = -0.41$ eV, $\mu_{\text{O}} = -0.95$ eV and D: $\mu_{\text{Sr}} = -4.54$ eV, $\mu_{\text{Cu}} = -0.19$ eV, $\mu_{\text{O}} = -1.17$ eV

Defects	A	B	C	D
Oxygen-excess				
$V_{\text{Cu}}' + h'$	1.29	1.29	0.88	1.10
Split $V_{\text{Cu}}' + h'$	2.12	2.12	1.71	1.93
$\text{O}_i'' + 2h'$	2.23	2.45	1.63	1.85
$V_{\text{Sr}}'' + 2h'$	1.34	1.77	0.96	0.96
Oxygen deficiency				
$V_{\text{O}}' + 2e'$	2.51	2.29	3.10	2.89
$\text{Sr}_i' + 2e'$	5.02	4.58	5.40	5.40
$\text{Cu}_i + e'$	2.54	2.54	2.95	2.73

possible value in the stability range (*i.e.* relatively strontium-rich conditions) and the oxygen chemical potential having its lowest possible value (oxygen-poor conditions). This combination of chemical potentials favours oxygen deficiency and indeed all oxygen-deficient defects possess lower formation energies than under condition A, C or D. However, oxygen-deficient defects are still between 1.00 and 3.27 eV higher in energy than the lowest energy oxygen-excess defect ($V_{\text{Cu}}' + h'$), hence a net oxygen-excess will result, dominated by copper vacancies.

Condition C is at the copper-poor, strontium-poor and oxygen-rich limits of the stability region ($\mu_{\text{Cu}} = -0.41$ eV, $\mu_{\text{Sr}} = -4.54$ eV and $\mu_{\text{O}} = -0.95$ eV). We would hence expect that these are the optimum conditions for oxygen-rich SrCu₂O₂ as this would result in the lowest possible formation energies for copper vacancies, strontium vacancies and oxygen interstitials. Indeed this is the case and results in the oxygen-rich defects lying in the range 0.88–1.71 eV while the oxygen-deficient defects are all higher in energy in the range 2.95–5.40 eV. These conditions should thus result in the greatest possible oxygen-excess and hence p-type conductivity. The lowest energy individual defect is $V_{\text{Cu}}' + h'$ with a formation energy of 0.88 eV with $V_{\text{Sr}}'' + 2h'$ also having a low formation energy of 0.96 eV.

Condition D corresponds to strontium-poor conditions ($\mu_{\text{Sr}} = -4.54$ eV) with Cu and O chemical potentials in the intermediate range ($\mu_{\text{Cu}} = -0.19$ eV, $\mu_{\text{O}} = -1.17$ eV). This lowers the energy of strontium vacancies relative to other defects so that they become the lowest energy defect. $V_{\text{Cu}}' + h'$ also has a low formation energy of 1.10 eV. Oxygen-deficient defects remain as the highest energy defects and are thus unlikely to form as hole-killer defects.

Thus the lowest energy defect varies with chemical potential with $V_{\text{Cu}}' + h'$ dominating the defect structure under most conditions although $V_{\text{Sr}}'' + 2h'$ can become the lowest energy defect under certain conditions.

B. Defect levels

Although energetic analysis allows us to predict the most stable defects, it does not tell us which of these, if any, will result in conductivity. It is therefore of importance to examine the changes in electronic structure that result from defect formation. Defects which result in good p-type conductivity should possess single particle levels near the valence band maximum which result in p-type conductivity through hole-hopping, while successful n-type conductivity requires the relevant defects to have electron donor levels near the conduction band minimum. Fig. 7 illustrates the positions of the single particle levels (SPLs) within the band gap of SrCu₂O₂.

The two lowest energy p-type defects, copper and strontium vacancies, both have single particle levels located just above the VBM. For $V_{\text{Cu}}' + h'$ one hole state is produced 0.09 eV above the VBM while for $V_{\text{Sr}}'' + 2h'$ two hole states occur—the lowest at the VBM and the second located 0.15 eV above the VBM. $\text{O}_i'' + 2h'$ produces a number of SPLs inside the band gap. Six of these are occupied by the electrons of the inserted oxygen while two hole states are located 1.13 and 1.45 eV above the valence band. As these are very deep in the band gap, oxygen interstitials can be expected to have a high activation energy for conduction. The position of the SPLs combined with their high formation energies suggests that oxygen interstitials are an unlikely contributor to

Fig. 7 Positions of single particle levels in band gap of SrCu_2O_2 at the Γ point. Empty circles indicate holes and arrows indicate electrons in up/down spins.

p-type conductivity in SrCu_2O_2 . Split vacancies result in two SPLs above the VBM and two unoccupied SPLs below the CBM. The two SPLs above the VBM consist of a filled state and an empty hole state. As the split vacancy consists of a combination of two copper vacancies and an interstitial copper ion, the two SPLs near the VB can be considered as resulting from the two vacancies while the SPLs near the CB arise from the interstitial.

Electron donor defects can introduce n-type conductivity if their SPLs occur close to the CBM. Fig. 7 suggests that $\text{Sr}_i'' + 2e'$ could induce n-type conductivity as it introduces two electrons into the bottom of the conduction band. However, $\text{Sr}_i'' + 2e'$ is the highest energy defect under all conditions, hence the electrons produced will always be charge-compensated by holes from the acceptor defects and it will not cause n-type conductivity. $\text{Cu}_i' + e'$ results in two filled SPLs above the VBM, one filled SPL 0.59 eV below the CBM and one empty SPL 0.46 eV below the CBM. This defect may cause n-type conductivity through the excitation of an electron into the conduction band. However, the existence of SPLs near the VBM is unexpected for this defect. The explanation for these levels lies in the underlying defect structure. Fig. 8 illustrates the relaxed geometry of the Cu interstitial defect. The inserted Cu atom relaxes towards a lattice Cu to form a Cu–Cu dimer. The defect can thus be described in Kroger–Vink notation as $V_{\text{Cu}}' + 2\text{Cu}_i'$. The SPLs above the VBM thus result from the formation of V_{Cu}' with those near the CBM resulting from the Cu dimer. $V_{\text{O}}'' + 2e'$ cannot cause n-type conductivity in SrCu_2O_2 as its donor SPL occurs deep in the band gap 0.22 eV above the VBM.

Fig. 8 Relaxed geometry of the inserted $\text{Cu}_i' + e'$ defect. Blue atoms indicate the Cu dimer that results.

Fig. 9 Relaxed geometry of $V_{\text{Cu}}' + h\bullet$ with blue atom indicating vacancy. Light blue isosurface illustrates the electron density of the defect band located 0.09 eV above the VBM at isosurface level of $0.05 \text{ e}\text{\AA}^{-3}$.

C. Electronic structure of $V_{\text{Cu}}' + h\bullet$

The local structure surrounding a copper vacancy is shown in Fig. 9. The oxygen ions neighbouring the vacancy have lost coordination from 3- to 2-fold coordinate and relax away from the vacancy by 0.24 Å due to Coulombic repulsion. The two copper ions nearest to the vacancy also relax away by 0.11 Å while the four nearest-neighbour strontium ions relax towards the vacancy by 0.13 Å.

Fig. 10 shows the band structure for $V_{\text{Cu}}' + h\bullet$. An empty SPL is seen in the band structure located 0.09 eV above the VBM at the Γ point. This can also be seen in the calculated EDOS (not shown here) which indicates the defect state to be composed of

Fig. 10 Band structure for $V_{\text{Cu}}' + h\bullet$ defect showing (a) α -spin and (b) β -spin bands. The dashed line indicates highest occupied level. Red line indicates defect acceptor band.

Table 5 Bader charges for acceptor state located 0.09 eV above the VBM for $V_{\text{Cu}}' + h'$ defect

Atom	Bader charge/e
Sr_{tot}	0.00
Cu_{tot}	0.67
O_{tot}	0.33
6 Cu	$2 \times 0.13, 4 \times 0.05$
2 O	2×0.08

hybridised Cu 3d and O 2p states. The electron density of this band is shown in Fig. 9. The hole state is spread across six Cu and two O ions with a larger density on the ions near the vacancy. Bader analysis of the empty defect state (Table 5) reveals it is composed of 67% Cu and 33% O. The degree of localisation (Fig. 9) suggests a polaronic-hopping conduction mechanism.

D. Electronic structure of $V_{\text{Sr}}'' + 2h'$

The relaxed geometry surrounding a Sr vacancy is shown in Fig. 11. Removal of an Sr ion results in the loss in coordination of two oxygen from 3- to 2-coordinate and their relaxation away from the vacancy by 0.33 Å. The two Sr ions neighbouring each of these oxygens relax towards them by 0.20 Å.

The band structure for the Sr vacancy is shown in Fig. 12. Two acceptor bands are seen in the spin down component of the band structure. The lower acceptor band (band I) lies across the top of the valence band and crosses the Fermi level which would result in metallic conduction, in contrast to the known activated conduction model. This may be due to a failure of the GGA + U methodology suggesting that further investigation with hybrid-DFT methods may be necessary to determine the correct defect structure. The upper SPL (band II) is split off from the valence band by 0.15 eV. The EDOS (not shown here) shows these levels to be composed of a mixture of Cu 3d and O 2p states.

Bader analysis for each of the SPLs is shown in Table 6. The atoms nearest to the vacancy appear to have the most density with 8 Cu atoms neighbouring the vacancy sharing 0.40% of the charge. The partial charge density for this band is shown in

Fig. 11 Structure of $V_{\text{Sr}}'' + 2h'$ in SrCu_2O_2 with blue atom indicating Sr vacancy. **Fig. 12** Band structure for $V_{\text{Sr}}'' + 2h'$ showing (a) α -spin and (b) β -spin bands. The dashed line indicates highest occupied level and red lines are unoccupied acceptor bands.**Table 6** Bader charges (in %) for acceptor bands (band I at VBM and band II 0.15 eV above VBM) induced by $V_{\text{Sr}}'' + 2h'$ indicating total Sr, Cu and O charges and charges on Cu ions near the vacancy

Atom	Band I	Band II
Sr_{tot}	0.00	0.00
Cu_{tot}	0.73	0.72
O_{tot}	0.27	0.28
Cu	8×0.05	4×0.13

Fig. 13a and shows the density to be localised over 8 Cu ions near the vacancy. Band II is again spread over several copper and oxygen ions. However, in this case there is a greater degree of localisation with 4 Cu ions each having a charge of 0.13 e so that they account for 0.52 e of the total charge. The partial charge density for band II is shown in Fig. 13b and shows the density to be spread over 4 Cu ions near the vacancy in a tetrahedral arrangement.

VI. Discussion

The apparent difference between the optical band gap and the fundamental band gap of SrCu_2O_2 has important implications for further theoretical studies of this material. The “fitting” of U values (or amounts of exact Hartree exchange in the case of hybrid functionals), to the experimental band gap of oxides, has become increasingly more common in recent years.^{74,75} Fitting to the band gap using GGA + U is only warranted for Mott insulators where the gap originates from the splitting of states of the same nature. In fact some researchers still employ *a posteriori* corrections, such as the “scissors operators” to correct the obvious problems GGA/LDA functionals have in predicting defect levels relative to “correct positioning” of the band edges.⁷⁴

Fig. 13 Partial charge density for defect states located (a) at VBM and (b) 0.15 eV above VBM at isosurface level of $0.08 \text{ e}\text{\AA}^{-3}$.

Our results indicate that there is $\sim 0.5 \text{ eV}$ of a difference between the optical band gap and the fundamental direct band gap. Applying this rationale to the known experimental optical band gap of $\sim 3.3 \text{ eV}$ leads to the conclusion that the fundamental direct Γ – Γ band gap could be as small as 2.8 eV . Thus fitting to a direct band gap of $\sim 3.3 \text{ eV}$ is not best practice. A similar result has been seen for the n-type TCO In_2O_3 , which has an optical band gap of 3.75 eV . A first principles investigation in synergy with X-ray spectroscopic techniques, conducted by Walsh *et al.*, has shown that the valence band-edge of In_2O_3 is significantly closer to the CBM than expected based on the optical band gap of 3.75 eV .⁵ Computational analysis of the direct optical transitions explains this discrepancy, showing that VB–CB allowed transitions only occur from bands 0.8 eV below the VBM, which sets an upper bound on the fundamental gap of 2.9 eV .⁵ This result calls into question any defect studies of In_2O_3 , where a 0.8 eV change in the band gap would have a significant effect on the position of defect levels relative to the true band-edge positions, especially in clarifying the description of defect levels as shallow or deep.^{74,75} Thus in the case of SrCu_2O_2 , comparison of the experimental optical gap to the fundamental direct gap obtained from calculations is not the correct approach.

This study also represents the first comprehensive analysis of the intrinsic defects of SrCu_2O_2 . We demonstrate that GGA is unsuitable to treat defects in this material as it results in the incorrect delocalisation of hole states, and predicts metallic conduction. These results call into question the use of GGA/LDA to model p-type defects in Cu(I) based TCOs, as the conductivity in these materials is known to be governed by polaronic-hopping mechanisms.^{76–78} Indeed, this study represents the only “beyond LDA/GGA” study at present on defects in these technologically important materials, as all previous studies have utilised LDA/GGA to investigate the defects in SrCu_2O_2 and Cu(I) based delafossites.^{37,79,80} GGA + U produces distinct acceptor levels in the band gap for most of the defects, consistent with the activated conductivity noted experimentally.^{20,25} However, for $V_{\text{Sr}}'' + 2h'$ GGA + U a defect level crosses the Fermi level resulting in metallic conduction. This indicates that for this material the GGA + U methodology is not completely adequate and that further studies with methods such as hybrid-DFT may be necessary to fully understand the defect structure.^{51,81}

One explanation for the poor conductivity in SrCu_2O_2 is the relatively high effective mass of the VBM which results in poor p-type conductivity. It is clear from the curvature at the VBM (Fig. 4) that SrCu_2O_2 does not possess the necessary dispersion for good p-type conduction, therefore it is not surprising that the effective masses of the VBM are so high. Conductivity in SrCu_2O_2 occurs *via* a polaronic-hopping conduction mechanism rather than a band conduction mechanism so the effective mass may not be as important in this case. In order to improve conductivity it is necessary to change the nature of the VBM, perhaps through the introduction of dopants such as Ca.³¹ This may result in lower effective masses at the VBM and may alter the conduction mechanism so that it is more band-like in nature similar to conduction mechanisms in n-type TCOs. Further experimental and theoretical work on dopants is thus of importance to attempt to optimise conductivity in this material.

Analysis of defect formation energies shows the importance of consideration of chemical potentials in this material. Omission of these leads to the mistaken conclusion that oxygen interstitials are the most stable defect, with Sr interstitials also having low formation energies and Sr vacancies appearing to be very high in energy. However, due to the narrow range of chemical potentials under which SrCu_2O_2 is stable which correspond to relatively Sr-poor, Cu-rich and O-poor conditions, we have shown that the most stable defects are Cu vacancies and Sr vacancies which will form to a differing extent depending on the chemical conditions. Oxygen-excess is favoured under all conditions within the stability range of SrCu_2O_2 , with oxygen-deficient defects unlikely to form.

Combining the energetics with the positions of the SPL indicates that both $V_{\text{Cu}}' + h'$ and $V_{\text{Sr}}'' + 2h'$ are likely to lead to p-type conductivity through acceptor states located above or near the valence band maximum. These were shown to be localised on several Cu and O ions in agreement with an activated hole-hopping mechanism of conductivity. This is consistent with the activation energy of 0.236 eV seen experimentally.²⁵ While strontium and copper interstitials do introduce defect levels suitable for n-type conductivity, it is highly unlikely to occur in SrCu_2O_2 due to the high formation energies of these defects.

VII. Conclusion

Stoichiometric and intrinsically defective SrCu_2O_2 were investigated using GGA corrected for on-site Coulombic interactions (GGA + U). The fundamental band gap of SrCu_2O_2 is found to be ~ 0.5 eV smaller than the optical band gap, due to transitions between the valence band maximum and conduction band minimum being symmetry disallowed. Analysis of the formation of intrinsic defects in SrCu_2O_2 tells us that n-type (oxygen-deficient) defects are unlikely to form, and that p-type (oxygen-excess) defects are favoured under all growth conditions. Our results indicate that both $V_{\text{Cu}}' + h^\cdot$ and $V_{\text{Sr}}'' + 2h^\cdot$ can cause distinct acceptor levels above the VBM, consistent with the activated conductivity reported experimentally, and are the probable cause of p-type conductivity in this material.

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