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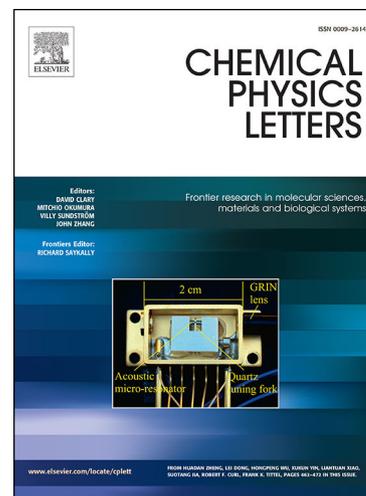
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# Strain or Electronic Effects? - The Influence of Alkali Metals on the Bandgap of $\text{Cu}_2\text{O}$

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## Abstract

Using density functional theory we studied the influence of group 1 and 11 impurities on the bandgap of  $\text{Cu}_2\text{O}$ . Our results show that dopants affect the bandgap through geometric and electronic effects. Geometric effects originate from the compression of adjacent Cu–O bonds while electronic effects are tightly connected to changes in the ability to delocalize electrons through 2 electron 3 center bonds. Doping with alkali metals disturbs the delocalization network and therefore results in an increased bandgap. The 2 electron 3 center bonding network is restored by Au and Ag dopants or decreased doping concentrations.

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## 1. Introduction

Cuprous oxide is an intrinsic p-type semiconductor with a bandgap of 2.17 eV[1, 2] which renders it a promising material for transparent semiconductors[3–5] or photocathodes in water splitting.[1, 6–12] A possibility to tune the band-gap and thus, the performance of cuprous oxide is the addition of dopants.[4–8, 13–16] The increased or decreased bandgap can be associated mainly with two effects, the differences in ionic radii (geometric effects) and the direct changes

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to the electronic structure induced by dopants (electronic effects). Since typically both effects are present it is difficult to distinguish them in traditional studies[3, 6, 8, 9, 13, 17] which simply consider the influence of dopants within  $\text{Cu}_2\text{O}$ . Despite this limitation these studies offered already valuable insights but a more complete understanding on how geometric and electronic effects affect the bandgap is still missing. In an effort to separate these effects, a study which solely focused on geometric effects induced through straining the unit cell by up to  $\pm 10\%$  was performed.[18] In contrast to earlier work,[5, 19] the previously claimed importance of d10—d10 interactions could not be confirmed. Instead, it was found that both the valence band (VB) and conduction band (CB) edges are determined by Cu—O  $\sigma^*$  antibonding states. Only in the presence of extreme compressive strain the presence of direct Cu—Cu interactions through Cu 4sp orbitals was observed.[18]

Building on these insights, we will expand the analysis to also include electronic effects. This is achieved by considering the simplest possible case which is the replacement of Cu(I) by isovalent alkali metals, Ag or Au in a small 1x1x1 (25% doping with respect to Cu) and a larger 2x2x2 unit cell (3% doping with respect to Cu). This provides the opportunity to explore the influence of electronic effects in the absence of internal redox reactions. In the spirit of building a fundamental understanding from the simplest possible systems Cu vacancy formation was neglected.

## 2. Computational Details

The bandgaps of pure and doped  $\text{Cu}_2\text{O}$  were extracted from density functional theory (DFT) calculations performed using the Vienna Ab-initio Simulation Package[20] (VASP version 5.4.1). Initially, the unit cell and geometries of all considered materials were converged using the generalized gradient approximation (GGA) PBE[21] functional together with a plane wave cut-off of 450 eV and a smearing of 0.1 eV. The structures were assumed to be converged if the largest force on any atom was below 0.05 eV/Å. This was followed by single-

point calculations using the HSE06[22, 23] range-separated hybrid functional from which bandgaps and density of states (DOS) were extracted. Density overlap region indicators (DORI)[24] were computed from the electron density  
40 obtained from GPAW (version 1.4.0) single-point calculations at the converged VASP-PBE structures using a PBE functional in combination with a 0.17 Å grid density. In all cases only the valence electrons were treated explicitly while the core electrons were approximated within the projector augmented wavefunctions (PAW) method[25, 26].

45 The unit cell was converged using the minimal  $\text{Cu}_2\text{O}$  unit cell, which contains 4 Cu and 2 O atoms, with a  $5 \times 5 \times 5$  k-point set. The bandgap and DOS of pure  $\text{Cu}_2\text{O}$  was extracted from the minimal unit cell using a  $5 \times 5 \times 5$  k-point set for the subsequent HSE06 computation. Doping and vacancy formation was studied using both the minimal  $1 \times 1 \times 1$  cell where 1 Cu ion was replaced by the dopant  
50 (25% doping with respect to Cu; corresponds to 16.7 at%) and a larger  $2 \times 2 \times 2$  unit cell which contains 32 Cu and 16 O atoms where again one of the Cu ions was replaced by the dopant (3% doping with respect to Cu; corresponds to 2.09 at%). The latter system was modeled using a  $3 \times 3 \times 3$  k-point set for both the PBE and HSE06 calculations. The doping level of the  $2 \times 2 \times 2$  unit cell  
55 is reasonably close to that typically found in experimentally relevant systems where doping levels of the order of 1 at% have been reported in the case of Na doping.[13, 14, 27, 28] Higher doping levels have been found to result in the formation of alkali metal oxide phases rather than substitution of Cu[11].

### 3. Results and Discussion

60 Considering initially only doping of  $\text{Cu}_2\text{O}$  in the minimal  $1 \times 1 \times 1$  unit cell with fixed lattice parameters, we find an increase of the bandgap for all alkali metal impurities. For example replacing 25% Cu(I) by  $\text{Li}^+$  increases the bandgap from 1.95 eV for pure  $\text{Cu}_2\text{O}$  to 2.46 eV. Since Cu(I) and Li(I) have nearly equivalent ionic radii,[29] this increase of the bandgap can almost exclusively be  
65 associated with the presence of electronic effects. Moving towards larger cations,

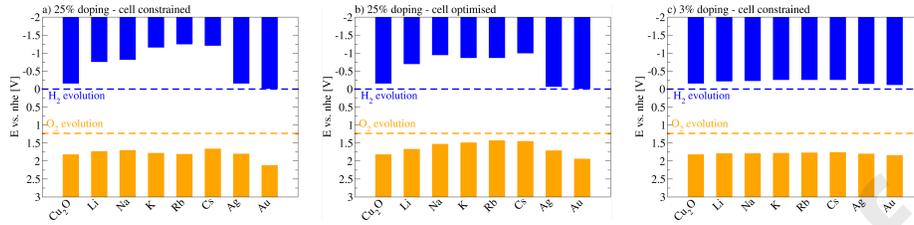


Figure 1: The bandgaps of pure and alkali metal doped  $\text{Cu}_2\text{O}$  are summarized. (a) 25% doping at unrelaxed  $\text{Cu}_2\text{O}$  unit cell; (b) 25% doping in relaxed unit cell; (c) 3% doping in unrelaxed unit cell. Band alignments are stated as electrochemical potentials (E) versus the normal hydrogen electrode (nhe).

also geometric effects start to be of relevance. Upon exchanging  $\text{Li}^+$  by the significantly larger  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Rb}^+$  ions an increase of the bandgap is observed with a maximum bandgap of 3.05 eV when doping with  $\text{Rb}^+$  (Figure 1a). The bandgap decreases again, compared to  $\text{Rb}^+$ , for a  $\text{Cs}^+$  impurity. Doping with  
 70 alkali metals has only a negligible effect on the VB edge whereas the CB edge is shifted towards higher energies (Figure 1a). This increase of the bandgap is in disagreement with experiments showing that it should not be affected by the presence of alkali metal impurities[14]. However Chen et al. considered significantly lower doping levels of approximately 0.7 at% compared to 16.7 at%  
 75 in the computations.

It is noteworthy, that the trends between the bandgap and the dopants' ionic radii align qualitatively with what has been found when applying external strain[18]. This is not surprising when considering the detailed changes in the geometries upon incorporation of differently sized alkali metals in the structure.  
 80 Substitution of Cu(I) results in a significant increase of the Dopant–O bond length compared to that of Cu–O in pure  $\text{Cu}_2\text{O}$ . This effect is only very minor for  $\text{Li}^+$  doping but it becomes more and more significant for larger dopants (see summary of the Dopant–O bond lengths in the supplementary information (SI)). This in turn results in a compression of the Cu–O bond lengths. For  
 85 example in the case of  $\text{Na}^+$  or  $\text{Cs}^+$  doping this bond is compressed by 5.1% and 7.8%, respectively. According to our earlier work,[18] this extreme strain should

result in a decrease of the bandgap. The absence of a decrease can be understood when considering that the distance between the Cu ions and the dopant is not affected by the presence of differently sized dopants, i.e. it remains 3.019 Å.

90 Due to this rather large interionic distance no interactions between the dopant and Cu 4sp states, which were responsible for the decrease of the bandgap under extreme compressive strain,[18] are possible. Indeed, both the VB and CB edges are determined by Cu–O  $\sigma^*$  interactions in all cases (see SI). In the light of the absence of such interactions it is also not surprising that the Cu–Dopant

95 distance remains constant since any changes would offset the Cu and/or the dopant ions from the high symmetry positions. This in turn would correspond to an energetically unfavorable disturbance of the O–Cu–O and O–Dopant–O angles away from the ideal linear ligand field. Having excluded the presence of direct interactions between the cations, the compression of the Cu–O bond

100 must be solely responsible for the geometric effects. Indeed, compressing this bond increases the overlap in the Cu–O covalent bond. This in turn enforces an increased energy gap between bonding, non-bonding and antibonding Cu–O states. Thus, the bandgap increases when moving from  $\text{Li}^+$  to  $\text{Rb}^+$ . Overall, the absence of any changes in the Cu–Dopant distance can be considered an

105 additional indication, that geometric effects resulting in the increased bandgap are solely determined by the compression of the Cu–O bond rather than earlier claimed d10–d10 interactions.[5, 19]

A possibility to isolate electronic effects is to repeat the calculation while allowing the unit cell to relax. Note that the calculations were constrained to

110 preserve the cubic unit cell. This results in an increase of the lattice parameters when doping with ions larger than Cu(I). Taking the most extreme case of Cs doping as an example, the unit cell parameters increase by 10% from 4.30 Å to 4.71 Å. Comparably smaller increases of the lattice constants are also observed for the other dopants. Relaxing the unit cell has also a profound influence on

115 the obtained bandgaps. Overall, we find the huge differences between the doped systems to almost vanish completely. Instead, a bandgap of approximately 2.3 eV is observed for all systems with a spread between 2.16 eV (Na doping)

and 2.43 eV (Cs doping; Figure 1b). Additionally, the differences between the dopants no longer follow any clear trends with respect to the ionic radii but  
120 instead are likely a result of the slightly different influence of the alkali metals on the electronic structure. This is not surprising considering that the Cu–O bond lengths of the doped oxide no longer differ significantly from that of pure Cu<sub>2</sub>O (see SI). Having removed a large part of the geometric effects we find an average increase of the bandgap of approximately 0.3 eV which can solely be  
125 associated with the presence of electronic effects.

From these results it is clear that the influence of Cu(I) exchange goes far beyond purely straining the Cu<sub>2</sub>O structure. In order to elucidate the origin of these electronic effects we decided to evaluate the electronic structure of alkali metal doped cuprous oxide in more detail. To obtain an initial qualitative  
130 understanding on how the presence of alkali metals in Cu<sub>2</sub>O affects the electronic structure we performed a density overlap region indicators (DORI)[24] analysis. This tool offers first insights whether a chemical bond is covalent or ionic.[30] The relevant DORIs are summarized in the SI and indicate, that the covalent bonding network between Cu and O, which is also present in pure Cu<sub>2</sub>O,[18, 31,  
135 32] is not disturbed by alkali metal dopants. The bond between dopant and O on the other hand significantly varies between the alkali metal impurities with DORI indicating the most covalent bonding character for Li<sup>+</sup> and the most ionic for Cs<sup>+</sup>. The covalent bonding between Cu and O is in good agreement with the Bader charges which indicate only a partial electron transfer from  
140 Cu to O, e.g. for pure Cu<sub>2</sub>O we find a charge of 0.67 on Cu rather than a full electron transfer. The change from a more covalent to an ionic bonding situation between the dopant and O indicated by DORI on the other hand does not agree with the removal of a full electron from Na or Li suggested by the Bader charges (see SI). Accordingly, the covalent bonding basin observed in the  
145 DORI may be an artifact resulting from taking the gradient of a rather small but localized electron density. The increased positive charge on the dopant results in a partial reduction of the Cu(I) ions as indicated by the slight decrease of the charges at Cu in the presence of Li<sup>+</sup>, Na<sup>+</sup> or K<sup>+</sup>. Larger cations on the other

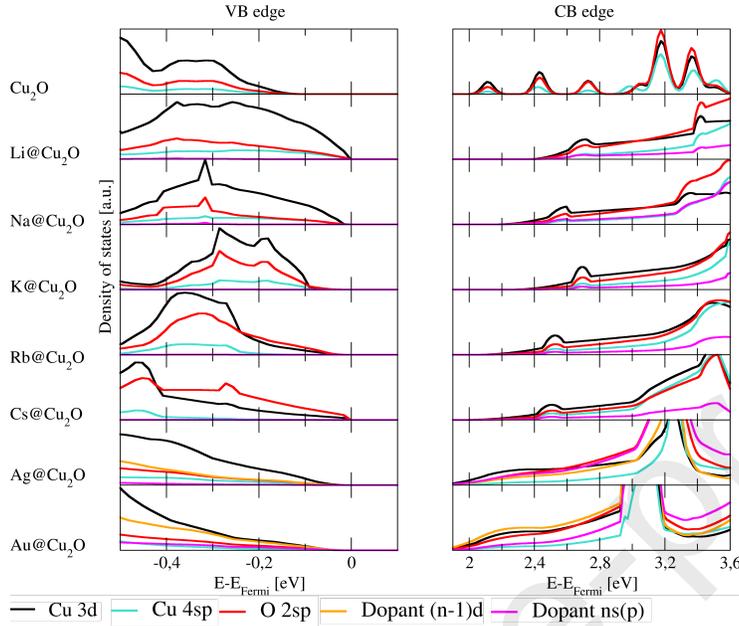


Figure 2: The partial density of states for pure and doped  $\text{Cu}_2\text{O}$  assuming 25% doping and an individually converged unit cell is depicted.

hand show a less pronounced ionic character, e.g. the charge on the dopant  
 150 decreases to 0.7 for  $\text{K}^+$  and 0.6 for  $\text{Rb}^+$  and  $\text{Cs}^+$ . Here, the "ionic" character  
 indicated by DORI may be a result of the easily polarizable valence shell of  
 these soft cations. The qualitative trends in the Bader charges of the dopants  
 are in disagreement with what has been reported by Caballero-Briones et al.[13]  
 earlier which indicate equal charges for all dopants. We therefore performed  
 155 additional GPAW/PBE single point calculations at the VASP/PBE geometry  
 which qualitatively confirmed the trends observed with VASP/HSE06 (see SI).

Overall neither the Bader charges nor DORI offers a first hint regarding the  
 origin of the electronic effects on the bandgap. In order to obtain a more diverse  
 picture we decided to analyze the electronic structure of the doped cuprites in  
 160 more detail using density of states (DOS). The DOS of the VB and CB edges  
 taken from calculations at the relaxed unit cell are shown in Figure 2. For pure  
 $\text{Cu}_2\text{O}$  it was earlier found that both the CB and VB edges are determined by

$\sigma^*$  antibonding orbitals formed by Cu 3d and O 2sp states which in turn form a network of delocalized 2 electron 3 center bonds (Figure 2).[18] Moving from  
165 pure to alkali metal doped  $\text{Cu}_2\text{O}$  we observe a relative shift of the CB edge towards higher energies. Apart from this, no significant qualitative changes in the VB or CB region are found. Identical to the pure oxide we find, that the CB and VB edges almost exclusively contain Cu 3d and O 2sp contributions with minor contributions from Cu 4sp. It is noteworthy that the dopant s-states are  
170 not present at the band edges and therefore are not involved in the delocalized 2 electron 3 center bonding network between Cu-O-Cu units. Having said this, it becomes clear that the addition of alkali metals disrupts the delocalization network spanned by the Cu-O-Cu multicenter bonds and enforces a partial localization, e.g. the number of Cu-O bonds through which the electrons are  
175 delocalized is reduced. Decreasing the length of the delocalization network in turn is known to result in a blue shift of the UV/Vis adsorption peak[33] which corresponds to an increased bandgap as observed for the doped systems at hand.

Following this argument, the bandgap of pure  $\text{Cu}_2\text{O}$  should be obtained again when restoring the delocalization or moving towards more realistic doping  
180 levels. The former can be achieved by replacing the alkali metal with monovalent cations which also contain d-orbitals which can participate in the Cu-O-Cu delocalization network. Natural choices to test this hypothesis are Au and Ag. Both elements display stable +I oxidation states combined with a full d-shell. Considering these similarities, replacing Cu by Ag or Au should only  
185 have a minor effect on the bandgap. For the non optimized 1x1x1 unit cell, this is indeed found for Ag doping which displays with 1.94 eV a bandgap which is almost identical to that of pure  $\text{Cu}_2\text{O}$  (Figure 1a). Doping with Au on the other hand results in a minor increase of the bandgap to 2.09 eV. This increase is most likely associated with the significantly larger ion size of Au[29]  
190 compared to Cu. Indeed, we observe a decrease of the bandgap to 1.75 eV when removing geometric effects through relaxing the unit cell. A similar decrease is also observed when optimizing the unit cell of the Ag doped oxide. This reduction of the bandgap can be associated with the presence of Ag or Au d-

states at both the CB and VB edges (Figure 2). Furthermore, Bader charges  
 195 indicate that the charge at Au and Ag is with 0.33 and 0.48 significantly lower  
 than that of Cu. This lower charge does not affect the surrounding Cu ions  
 but instead results in a less negative charge of -1.24 (Ag doped) and -1.19 (Au  
 doped) at the adjacent O atoms. This may indicate an increased covalent nature  
 of the Ag-O or Au-O bonds which in turn strengthens the delocalization through  
 200 Cu-O-Ag or Cu-O-Au bonds. Accordingly, the electronic effects should result  
 in a decrease of the bandgap which is indeed also found (Figure 1b).

Similar to the doping with +I charged transition metal ions also the in-  
 crease of the unit cell should dilute the disturbance of the Cu-O-Cu 2 electron  
 3 center bond network. Accordingly, a bandgap similar to that of pure Cu<sub>2</sub>O  
 205 could be expected despite doping with alkali metals. To test this hypothesis we  
 considered a 2x2x2 Cu<sub>2</sub>O unit cell with 32 Cu atoms. This corresponds to a  
 more realistic doping level of 3% versus Cu which is reasonably close to typical  
 dopant concentrations in experimentally relevant systems.[13, 14, 27, 28] In line  
 with our hypothesis we find only a very minor increase of the bandgap from  
 210 1.95 eV for pure Cu<sub>2</sub>O to 2.00 eV. This increase is independent from the choice  
 of alkali metal (Figure 1c) and agrees qualitatively with experimental observa-  
 tions for slightly lower dopant levels.[13, 14]. Accordingly, the experimentally  
 observed increased photocurrent[11] and decrease of the resistivity[27] are not  
 due to changes in the bandgap. Similarly also the bandgaps of Au and Ag doped  
 215 systems are no longer affected for the larger unit cell, e.g. a bandgap of 1.94 eV  
 is found. It is noteworthy that increasing the unit cell does not affect the VB  
 and CB edges in the DOS which are still determined by Cu 3d and O 2sp  $\sigma^*$   
 states (see SI). Similarly also the Au 5d and Ag 4d states are present at the VB  
 and CB edges for the 2x2x2 unit cell (see SI).

#### 220 4. Conclusions

In summary we were able to separate the electronic and geometric effects  
 on the bandgap induced by doping with alkali metals. The geometric effects

result, similar to moderate external compressive strain,[18] in an increase of the band gap. These changes are a direct result from the compression of the Cu–O bond. Electronic effects induce an additional increase of the band gap at 25% doping (1x1x1 unit cell) which is to a large extent independent from the choice of alkali metal. The insertion of alkali metals did not affect the electronic structure of the VB and CB band edges, i.e. they are identical to the undoped case still determined by delocalized Cu–O  $\sigma^*$  states. Instead, the increase of the bandgap induced by the electronic effects was associated with the disruption of the 2 electron 3 center bond network spanned by the Cu-O-Cu units. This hypothesis was verified by considering a larger 2x2x2 unit cell which increases the number of Cu-O-Cu moieties through which the electrons can be delocalized before a blocking alkali metal dopant is encountered. Accordingly, bandgaps similar to that of pure Cu<sub>2</sub>O are observed. Similarly also the introduction of d-orbitals through Ag and Au dopants restores the possibility for extended 2 electron 3 center bond networks. As a result a decrease of the bandgap compared to the alkali metal doped systems is again found.

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## Credit Author Statement

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**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

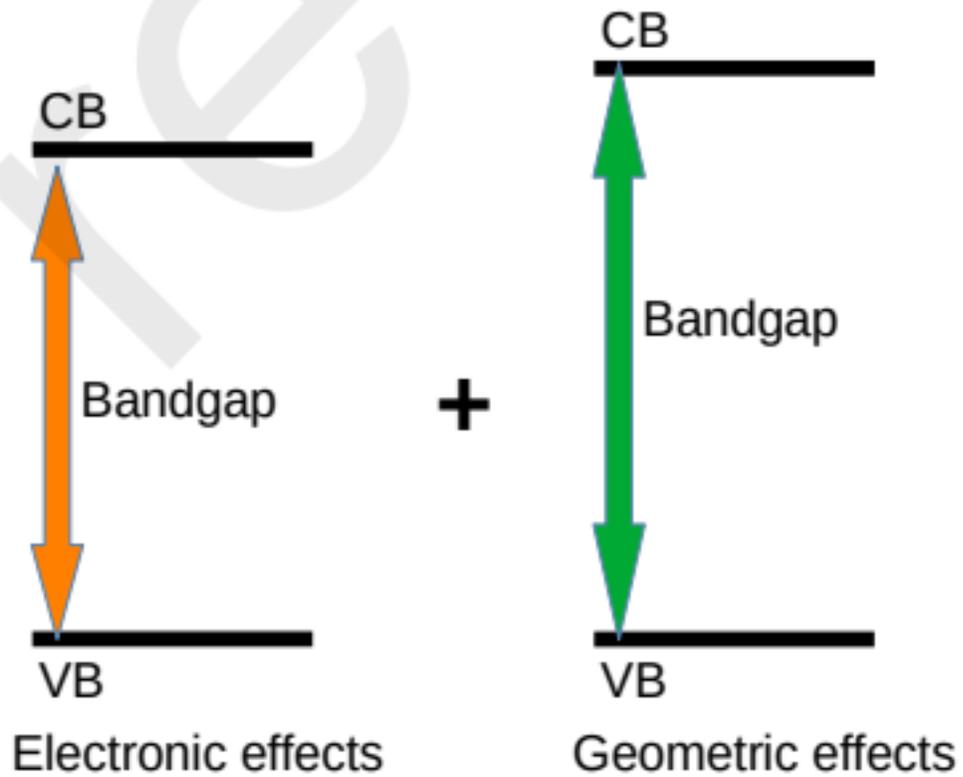
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Pure  $\text{Cu}_2\text{O}$



Group 1 Doping

Group 1 doped  $\text{Cu}_2\text{O}$



## Highlights

- Inert dopants influence bandgap of  $\text{Cu}_2\text{O}$  through geometric and electronic effects
- Geometric effects result from different ionic radii affecting the Cu-O bond length
- Electronic effects are induced by disturbing 2 electron 3 center bonding in  $\text{Cu}_2\text{O}$