Research Article

Electronic Structure of the CuCl$_2$(100) Surface: A DFT First-Principle Study

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First-principle density functional theory (DFT) and a periodic-slab model have been utilized to investigate the structure of the CuCl$_2$(100) surface. Structural parameters of the bulk CuCl$_2$ are reported and compared with the experimental values. The structure of the CuCl$_2$(100) is calculated using a (2 × 2) supercell. Structural parameters in terms of bond lengths and bond angle are calculated. Electronic properties of the CuCl$_2$(100) surface are investigated by calculating the density of state (DOS) and the projected density of state for a slab containing five layers.

1. Introduction

Copper plays a prominent role in many fields. This is primarily due to its unique mechanical properties and excellent electrical and thermal conductivity. Its applications span heating and cooling piping, heat exchanging, electrical appliances, architecture, and catalysis [1–6].

Adsorption of halides on metallic surfaces is of particular importance due to their relevance for many industrial processes and its role in the formation of notorious environmental pollutants such as dioxins [7]. Central to a comprehensive understanding of various phenomena such as corrosion, electrodeposition, and catalytic cycles is addressing adsorption of chlorine on copper surfaces on a precise atomic-scale.

Motivated by its diverse application, the chlorine-copper interaction has attracted great deal of experimental [8–14] and theoretical [15–18] studies. Mounting experimental evidence shows a strong interaction between Cl and Cu atoms as evident from electron diffraction (LEED) [8], normal-incident X-ray standing wave (NIXSW) [9], surface-extended X-ray adsorption fine structure (SEXAFS) [10, 11], shadow-cone-enhanced secondary-ion mass spectrometry (SIMS) [6, 12], and Scanning Tunnelling microscopy (STM) [13, 14] methods. STM studies found that the chlorine molecules adsorb dissociatively on the Cu(111) surface, leading to formation of various well-ordered phases. It is also found that Cl atoms prefer to adsorb onto face-centered cubic (fcc) hollow positions over the hexagonal close-pack (hcp) hollow, bridge, and top positions [13, 18].

Computational data for the Cl/Cu(111) system based on cluster [15] or a periodic DFT-based calculation [16, 17, 19] has been presented by different groups Doll and Harrison [16], Migani et al. [17], and Peljhan and Kokalj [19]. It was found that the preferred adsorption of the Cl atoms is the face-centered cubic (fcc) [16]. Peljhan et al. presented an extensive DFT calculation of Cl adsorption on Cu(111), considering a wide range of Cl coverages ranging from 1/16 to 1 ML. The strong interaction between Cl and Cu atoms results in the formation of two distinctive different materials; namely, CuCl and CuCl$_2$. The crystal structure of the CuCl$_2$ follows a base-centered monoclinic space group C2/m [20–22]. As demonstrated by Burns and Hawthrone [23]. Cu atoms are positioned in an axially distorted octahedral...
First-principle simulation, based on density functional theory (DFT), is now one of the key tools for studying and developing a key understanding of solid surfaces. DFT calculations can provide an atomic-based insight into the detailed bonding arrangement of structures, their energetic stability, and charge densities. To this end, this contribution investigates the electronic structure of the Copper (II) chloride, CuCl₂, mainly in the (100) surface orientation.

### 2. Methodology

The calculations reported in this paper have been performed using the plane wave pseudopotential density functional theory (DFT) method as implemented in the VASP program [24–27]. The generalized gradient approximation (GGA) for exchange and correlation as developed by Perdew and Wang (PW91) [28] was used to perform the spin-polarized calculations. Projector augmented wave (PAW) potentials [24, 25, 29] are used to represent the ionic potentials. A unit cell comprising four atomic layers has been employed together with a vacuum thickness of at least 14 Å to separate each slab from its neighboring images along the z-direction (normal to the surface). The three top-most layers of the slab were allowed to fully relax. The Brillouin-Zone (BZ) integrations were performed using automatic generation of $(3 \times 3 \times 1)$ and $(5 \times 5 \times 1)$ k-point set of Monkhorst-Pack random sampling [30]. Total energy was converged to an accuracy of $1 \times 10^{-3}$ eV. Deployed energy cut-off was set at 300 eV. The choice of this value, stems from the maximum value of the kinetic-energy for the Cl and Cu atoms, that is, 280 and 273 eV, respectively.

### 3. Results

#### 3.1. Bulk Properties.

CuCl₂ forms a base-centered Monoclinic Bravies lattice. As shown in Figure 1, each Cu atom is in an axially distorted octahedral environment with four equatorial nearest neighbors Cl atoms and two axial Cl atoms. The lattice constants were determined (as illustrated in Table 1) by plotting the variation in the energy with respect to the volume of the unit cell of bulk CuCl₂. The

<table>
<thead>
<tr>
<th>Reference</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\beta$ (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>7.35</td>
<td>3.40</td>
<td>7.20</td>
<td>117</td>
</tr>
<tr>
<td>Previous calculation (ref. [19])</td>
<td>7.52</td>
<td>3.35</td>
<td>7.29</td>
<td>119</td>
</tr>
<tr>
<td>Experiment (ref. [23, 31])</td>
<td>6.90</td>
<td>3.30</td>
<td>6.82</td>
<td>122</td>
</tr>
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</table>

There are two distinct bands in the valence region (Figure 2(a)). The Cu band (predominantly Cu 3d and little contributions of Cu (3p and 4s)) occupies the region (0 to $-5$) eV, and the Cl band (predominantly Cl (3s and 3p)) occupies that of ($-14$ to $-15$) eV. The surface state band resides just above the Fermi level where two regions are highlighted. The first one is in the region from 3.0 to 7.0 eV, while the second one is from 7.5 to 9.0 eV. The first region above the Fermi level is predominantly the empty state Cu 4s and the contribution in this region from Cu 3p and Cl (3s and 3p) is minimal (see Figures 2(b) and 2(c)). The second region above the Fermi level is predominantly the state Cu (3d and 3p) and Cl (3s and 3p).

#### 3.2. CuCl₂(100) Surface.

A supercell of the CuCl₂(100) is constructed from the optimized bulk unitcell and also based on the data in [21, 22, 32]; the unit cell is shown in Figure 3. This unit cell is a base-centered Monoclinic with one Cu atom located in the center of each base and four Cl atoms in the corner of each base. The Cu atom has four nearest neighbors Cl atoms in the same plane (plane of a and b) and two Cl atoms in c direction.
Figure 2: Density of state (DOS) of the bulk of the CuCl$_2$: (a) total DOS, projected DOS (PDOS) of (b) Cu atom and (c) Cl atom.

Test is performed using automatic generation of (3 × 3 × 1) and (5 × 5 × 1) $k$-point set of Monkhorst and Pack. For each optimization using these two schemes, the total energy was converged to an accuracy of $1 \times 10^{-3}$ eV and the forces on each ion to an accuracy of 0.015 eV Å$^{-1}$. A test using (5 × 5 × 1) $k$-point changed the total energies of the (3 × 3 × 1) $k$-point by only few meV. All the calculations discussed here are using a 3 × 3 × 1 $k$-point grid (unless otherwise specified).

Transformation upon building the surface can be viewed in terms of the relaxation, that is, the change in interatomic distances and angle $B$ between optimized bulk unit cell and the extended surface. We found that Cu-Cl distances become longer in the extended surface than the bulk one by only 0.009 Å. While the angle $B$ on the unit cell unit cell varies between 117° in the bulk and 111.3° in the surface (as shown in Figure 3). It is worthwhile also mentioning that optimized surface retains the symmetry exhibited by the unit cell. A noticeable difference in $c$ and $a$ lattice constants could be rationalized based on the shortcoming of standard DFT methods in describing states relating to long-term weak interactions (Van der Walls type) [33, 34].

The surface has a space group C2/m (as shown in Figure 3) the same as that of the CuCl$_2$ bulk. Unit cells are shifted from each other by 4.06 Å. The super-cell of the surface is illustrated in Figure 4; the top and side views are also shown in Figure 5. All bond lengths and bond angles are illustrated in Table 2 based on Figure 5(b). The distance between each two atomic layer is 3.212 Å. The surface has been optimized also by the (5 × 5 × 5) $k$-point set, and some of the bond lengths and bond angles are illustrated also in Table 2 based on Figure 5(b). As can be noticed from Table 2,
some of the bond length shrinks slightly by 0.02 Å while the others stay the same. Also some of the bond angle did not change, while the others changed by only 0.2°. Angle B in the unit cell illustrated in Figure 3 becomes smaller also by 0.8°.

3.3. Electronics Properties. The electronics properties of the CuCl$_2$(100) surface are investigated by calculating the density of state (DOS) for a slab containing five layers using the automatic generation of $(3 \times 3 \times 1)$ $k$-point. Figure 6 shows the total DOS and projected DOS of the surface. The investigation of the DOS shows that there are three main regions in the valence band below the Fermi level (0 eV in Figure 6(a)). The first and second regions occupy the regions of ($-2$ to $-6$) eV and ($-6$ to $-8$) eV. These two regions are mainly composed of Cu 3d (Figure 6(b)), with a little contribution of Cl 3p, but the Cu (4s and 3p) and Cl 3s states are minimal (Figures 6(b) and 6(c)).

The last region in the valence band is starting at $-17$ eV; it is composed of Cl 3s states. The conduction band has
8.27

Cl1 Cl2

Cl3 Cl4

Cl5 Cl6

Cu1 Cu2

Cu3 Cu4

To p v i e w

Figure 5: (a) Side view and (b) top view of the CuCl2(100) surface; Figure 5(a) shows part of the surface in Figure 5(b) but rotated to show
the structure. Dimensions are in angstrom.

Table 2: Calculated structural parameters of the CuCl2(100) surface using (3 × 3 × 1) and (5 × 5 × 1) k-point set of Monkhorst and Pack,
angle B is the one in the unit cell as in Figure 3.

<table>
<thead>
<tr>
<th>Bond length (Å)</th>
<th>(3 × 3 × 1)</th>
<th>(5 × 5 × 5)</th>
<th>Bond angle (°)</th>
<th>(3 × 3 × 1)</th>
<th>(5 × 5 × 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu1–Cl1</td>
<td>2.287</td>
<td>2.275</td>
<td>Cu1–Cl1–Cu2</td>
<td>94</td>
<td>94</td>
</tr>
<tr>
<td>Cl1–Cu2</td>
<td>2.280</td>
<td>2.273</td>
<td>Cl1–Cu2–Cl3</td>
<td>93.8</td>
<td>94</td>
</tr>
<tr>
<td>Cu1–Cl3</td>
<td>2.270</td>
<td>2.270</td>
<td>Cl1–Cu1–Cl3</td>
<td>86</td>
<td>86</td>
</tr>
<tr>
<td>Cl1–Cu1</td>
<td>2.270</td>
<td>2.275</td>
<td>Cl1–Cl1–Cu2</td>
<td>94</td>
<td>94</td>
</tr>
<tr>
<td>Cu1–Cu3</td>
<td>7.190</td>
<td>7.190</td>
<td>Cl1–Cu2–Cl3</td>
<td>86.2</td>
<td>86</td>
</tr>
<tr>
<td>Cl3–Cl3</td>
<td>4.090</td>
<td>4.090</td>
<td>B</td>
<td>111.3</td>
<td>110.5</td>
</tr>
<tr>
<td>Cu2–Cu4</td>
<td>7.190</td>
<td>7.190</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Cl4–Cu6</td>
<td>4.080</td>
<td>4.080</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

two distinct regions starting at 1.5 eV with a wide of approximately 2.5 eV for each one. Each of these regions has small peaks at 3.2 eV and 5.2 eV, respectively. The first region is predominantly Cu (4s and 3p) and Cl (3s and 3p), while the second region is predominantly of Cu 4s and the Cl (3s and 3p).

4. Conclusions

The structural, electronic properties of bulk and (100) surface of CuCl2 were investigated by means of periodic quantum chemical calculation based on the first-principle DFT approach. For the bulk, the comparison of optimized structural parameters with experimental and previous DFT study shows that the lattice constants are in a good agreement. The supercell of the CuCl2(100) surface showed to be axially distorted in the z direction. The interlayer distance, all the bond lengths, and the bond angle are calculated.

Total and projected Density of State (DOS) for the bulk and the extended surface is calculated. For the (100) surface, the valence band is having two regions: the first one composed of Cu (3d) and Cl (3p), while the second region is composed of Cl (3s) states. The surface states above the Fermi level are composed of manly Cu (4s and 3p) and Cl (3s and 3p). An extension to this work is to study the adsorption and dissociation of small molecules such as H2 and H2O on this surface.
Figure 6: Density of state (DOS) of the CuCl$_2$(100) surface: (a) total dos, (b) projected DOS (PDOS) of the surface Cu atom, and (c) projected DOS (PDOS) of the surface Cl atom.

References


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