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Structures, Electronic Properties and Stability Phase Diagrams for Copper (I/II) Bromides Surfaces

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Abstract

This study presents a comprehensive periodic-slab DFT investigation into structures, electronic properties and thermodynamic stability of all plausible terminations of CuBr and CuBr₂ surfaces. We first estimate lattice constants, formation and cohesive energies for the two bulk copper bromides before proceeding to analyse geometrical and electronic features of CuBr and CuBr₂ configurations. Surface geometries exhibit, to a large extent, corresponding bulk structures. Nevertheless, certain CuBr₂ surfaces experience a downward displacement of the topmost Cu-containing layers. We plot total and projected density of states for bulk and surface geometries of these two copper bromides and calculate their associated Bader’s electronic charges. Electronic structure analysis for bulk and surfaces of these two copper bromides show that CuBr bulk and its most stable surface (CuBr(111)_CuBr) do not exhibit any metallic character, while CuBr₂ bulk and its most stable surface (CuBr₂(001)_Br ) both exhibit metallic characters. The formalism of the ab initio atomistic thermodynamics affords the construction of energy phase diagrams. We predict the CuBr(001) surface, truncated with Br atoms, to be the most stable structure among all considered CuBr slabs at all physically meaningful ranges of the chemical potential of bromine. This surface resembles a c(2 × 2)-bromine sheet, that was characterised experimentally from initial interaction of Br₂ with a Cu(100) surface. We find that surfaces terminated with the electronegatively-charged bromine atoms, if accompanied with significant relaxations, tend to be more stable. Calculated surface energies serve to predict the shapes of CuBr and CuBr₂ nanoparticles as the chemical potential of bromine changes.
1. **Introduction**

A wide array of industrial and environmental applications drives the research into the interaction of halogens (Cl, Br) with copper surfaces. For example, adsorption of halogens on copper surfaces finds frequent applications in microelectronics industry.\(^1\) Copper bromides serve as important intermediates in the synthesis of polymers. On the other hand, copper halides play a crucial role in the chlorination mechanism of the environmentally notorious dioxin compounds.\(^2,3\) The halogenation behaviour of copper surfaces depends primarily on the surface termination and the load of gaseous halogen.\(^4-10\) Under conditions of ultra high vacuum (UHV), adsorption of chlorine and bromine on copper surfaces results in well-ordered configurations. van der Waals diameters of bromine and chlorine atoms represent a dominant factor in determining the final saturation structures.\(^4\) Various experimental\(^11\) and theoretical approaches\(^12,13\) have served to investigate the adsorption of chlorine on low-index copper surfaces. However, adsorption of bromine on copper surfaces has generally received less attention.

Temperature programmed desorption measurements by Nakaura et al.\(^5,6\) revealed that etching of a Cu(100) surface by Br\(_2\) take place in two steps. The first step comprises formation of a hexagonal pattern, observed by low-energy electron diffraction (LEED), attributed to a film layer of copper (I) bromide (CuBr). The layer becomes unstable and sublimes around 400 K, mainly in the form of Cu\(_3\)Br\(_3\). LEED measurements indicated immediate dissociation of gaseous bromine molecules leading to the formation of a saturated \(c(2 \times 2)\) sheet that corresponds to a coverage of 0.50 monolayer (ML).\(^6\) Further exposure of this layer to Br\(_2\) results in the formation of bulk CuBr. However, putative surface mobility of Br adatoms prevented conclusive imaging of the \(c(2 \times 2)\) layer by scanning transmission microscopy
Similarly, Jones and Kadodwala studied the dissociative chemisorption of Br₂ on a Cu(111) surface by means of several experimental techniques. They found that the maximum possible coverage amounted to 0.41 ML and exhibited a \((9\sqrt{3} \times 9\sqrt{3})R30^\circ\) arrangement.

Theoretically, Kenny et al. estimated binding energies of Br atoms on a Cu(100) surface at low coverages predicting the adsorption on a hollow site to be slightly more stable than that on a bridge site. Rampulla et al. reported very low activation energies for diffusion of bromine atoms on ideal and stepped copper surfaces. In order to explain the unusual ability of STM imaging to capture a highly mobile Br atom on a Cu(100) surface, Kenny et al. postulated that, Br atoms bind to copper vacancy sites, rather than to hollow sites on the surface. If compared with a Cl/Cu(100) system, Suleiman et al. demonstrated from thermodynamic calculations that, pure on-surface adsorption of Cl atoms dominates the substitutional adsorption.

While studies on chlorine adsorption on copper surfaces indicate the co-existence of copper (I) chloride (CuCl) and copper (II) chloride (CuCl₂) on the surface, corresponding studies on bromine adsorption did not confirm the formation of copper (II) bromide (CuBr₂). In an analogy to copper-chlorine systems, formation of bulk CuBr and CuBr₂ represents limiting cases for adsorption of gaseous bromine on copper surfaces. A recent study has investigated the role of CuBr₂ in the so-called “de novo” formation of polybrominated dibenzo-\(p\)-dioxins and polybrominated dibenzofurans. CuBr₂ acts not only as a bromination agent via electrophilic substitution, but also accelerates the degradation of the carbonaceous structure. Several investigations reported the strong bromination properties of CuBr₂ for ketones, alcohols, aromatics and other substrates in cross-coupling reactions. Despite
their importance in formation of brominated pollutants and synthesis of organic chemicals, literature provides no data pertinent to structural configurations and energies of any of the CuBr or CuBr$_2$ surfaces.

In this paper, we deploy the density functional theory (DFT) applied to periodic slabs to investigate structures of copper bromide surfaces. We aim (i) to report structural, thermochemical and electronic properties of bulk CuBr and CuBr$_2$, as well as (ii) to provide geometries of all plausible terminations of CuBr and CuBr$_2$ surfaces and (iii) to assess their thermodynamic stability under practical conditions of temperature and pressure.

2. Methodology

2.1. Structural optimisation of surfaces

The VASP code $^{21}$ served to carry out all structural optimisations and energy calculations based on the PAW-GGA functional $^{22}$. We modelled CuBr and CuBr$_2$ surfaces using 1 by 1 surface supercells consisting of 12 to 26 symmetric-slab layers (containing 26 to 104 atoms). Utilisation of symmetric structures (i.e., slabs with two uppermost layers) eliminates surface deformation that might be caused by accumulation of dipole moment along the $z$-direction, especially for the case of polar constructions $^{23}$. During optimisations, all atomic layers were allowed to relax. Vertical vacuum regions of 15.0 Å to 20.0 Å separated surfaces from their neighbouring images along the $z$-direction (on the two sides of the symmetric slabs). In all simulations, we set the energy cut-off to 400 eV. We exploited Monkhorst-Pack (MP) $^{24}$
schemes to perform integrations of the Brillouin zone (BZ), resulting in 9-10 \( k \)-points in the irreducible part of the BZ for all surfaces.

Optimisation of one structure (CuBr\(_2\)(101)\_Br, see Section 3.2), using an energy cut-off of 500 eV and 15 \( k \)-points, changes its total energy by only 6.0 meV. The precision of total energies and forces on each ion converge to \( 10^{-6} \) eV and \( 10^{-4} \) eV Å\(^{-1} \), respectively. We optimised each slab using spin-polarised and spin-unpolarised plane-waves. Then, we considered the minimum energy structure from these two sets of calculations. While the difference in energy between spin-polarised and spin-unpolarised calculations is rather negligible for most of the structures (i.e. 0.00 – 0.09 eV), it reaches values as large as 1.43 eV for one surface (CuBr\(_2\)(110)\_Br, see Section 3.2).

2.2. Calculations of bulk CuBr and CuBr\(_2\)

We optimise bulk unit cells of CuBr and CuBr\(_2\) using an energy cut-off of 600.0 eV and a \( 6 \times 6 \times 6 \times 6 \) MP scheme for generation of \( k \)-points. The enthalpy of formation \( (E^f) \) and cohesive energy \( (E^{coh}) \) for the two copper bromides are calculated according to:

\[
E^f = E^{\text{Bulk CuBr}} - E^{\text{Bulk Cu}} - \frac{n}{2}E^{\text{Br}} \quad E^{\text{coh}} = E^{\text{Bulk CuBr}} - E^{\text{gas Cu}} - nE^{\text{Br}}
\]  

(1)

where \( E^{\text{Bulk CuBr}} \) and \( E^{\text{Bulk Cu}} \) refer to energies of bulk copper bromides and copper, respectively, per unit formula. \( E^{\text{gas Cu}} \) and \( E^{\text{Br}} \) denote energy of isolated Cu and Br atoms, correspondingly, whereas \( E^{\text{Br}} \) signifies energy of a Br\(_2\) molecule.
We test the convergence in surface energies ($\gamma_{surf}$) with respect to the slab thickness on one structure, CuBr$_2$(101)$_\text{Br}$ (refer to section 3.2):

$$\gamma_{surf} = \frac{E_{slab} - N^{Bulk}E_{CuBr_2}}{2A}$$

(2)

where $E_{slab}$, $N^{Bulk}$, $E_{CuBr_2}$ and $A$ signify the calculated energy of the surface, energy of bulk CuBr$_2$ (per unit formula), number of bulk CuBr$_2$ units in the surface, and the surface area, respectively. We find that constructing the surface from seven and nine sheets of octahedral CuBr$_4$ blocks cause $\gamma_{surf}$ of the surface to differ by only 12.4 meV and 24.0 meV, correspondingly, in reference to utilising five sheets.

2.3. Bromine adsorption on a Cu(100) surface

We study in detail the structure of Cu(100) surface for adsorption of Br atoms, simulating it using a six-layer slab. We keep the two bottommost layers fixed at their bulk positions while allowing the remaining layers to relax. In these calculations, we adopt the same convergence criteria as illustrated above for the copper bromides surfaces. Our calculated geometries$^{25}$ of bulk Cu and the Cu(100) surface (i.e., lattice constant and surface relaxations) matches corresponding experimental geometries.

2.4. Ab initio atomistic thermodynamics

We construct energy phase diagrams incorporating all CuBr and CuBr$_2$ surfaces based on the approach of ab initio atomistic thermodynamics. Literature provides detailed account of the
Herein, we only refer to the final governing equations. In this procedure, the dependency of surface free energies, $\gamma(T, P)$, on temperature ($T$) and pressure ($P$) is expressed as:

$$\gamma(T, P) = \frac{1}{2A} \left[ G_{\text{surf}}(T, P) - N_{\text{Cu}} G_{\text{Cul}}(T, P) - (N_{\text{Br}} - nN_{\text{Cu}}) \mu_{\text{Br}}(T, P) \right]$$  \hspace{1cm} (3)

in which $G_{\text{surf}}(T, P)$ and $G_{\text{Cul}}(T, P)$ denote the Gibbs free energies for copper bromide surfaces and bulk copper bromides, respectively, at temperature and pressure of interest. $N_{\text{Cu}}$ and $N_{\text{Br}}$ denote the number of copper and bromine atoms in the slab, whereas $\mu_{\text{Br}}(T, P)$ designates the chemical potential of bromine:

$$\mu_{\text{Br}}(T, P) = \Delta \mu_{\text{Br}}(T, P) + \frac{1}{2} E_{\text{Br}^2}$$  \hspace{1cm} (4)

The change in chemical potential of bromine ($\Delta \mu_{\text{Br}}(T, P)$) readily follows from standard thermodynamic tables.\textsuperscript{29} After a series of simplified assumptions, one could write:\textsuperscript{28}

$$G_{\text{surf}}(T, P) = E_{\text{surf}}(0 \text{ K, 1 atm}) \quad G_{\text{Cul}}(T, P) = E_{\text{Cul}}(0 \text{ K, 1 atm})$$  \hspace{1cm} (5)

The two terms $E_{\text{surf}}(0 \text{ K, 1 atm})$ and $E_{\text{Cul}}(0 \text{ K, 1 atm})$ stand for the energies produced from DFT calculations. In consequence, the equation for $\gamma(T, P)$ represents a linear relation with respect to $\Delta \mu_{\text{Br}}(T, P)$. 

physical origin and the derivation of this formalism.\textsuperscript{26-28}
To ensure accurate k-point sampling, we deploy a $10 \times 10 \times 10$ MP k-point scheme in calculations of total density of states (DOS) and atomic projected density of states (PDOS). We construct Wulff shapes with the aid of the VESTA code. Finally, we calculate Bader’s charges by using a code developed by Henkelman’s group.

3. Results and Discussion

3.1. Bulk CuBr and CuBr$_2$

Figure 1 portrays unit cells for bulk CuBr and CuBr$_2$. Structures of these two units are akin to those of CuCl and CuCl$_2$. The CuBr unit cell assumes a zinc blende-like structure in which both Cu and Br atoms form an octahedral arrangement with identical Cu-Br distances of 2.38 Å. In the monoclinic structure of CuBr$_2$, each Cu atom resides in an axially distorted octahedral environment with two axial Br atoms (Cu-Br = 3.42 Å) and four nearest Br atoms (Cu-Br = 2.41 Å). Shortest Cu-Cu distances in CuBr and CuBr$_2$ unit cells amount to 3.89 Å and 3.48 Å, correspondingly.

Table 1 enlists calculated lattice constants, $E^f$ and $E^{coh}$ values of bulk CuBr and CuBr$_2$. Our calculated lattice constant for bulk CuBr (5.796 Å) coincides with the experimental measurement (5.696 Å). While our estimated $b$ lattice constant of CuBr$_2$ (3.437 Å) concurs with its experimental determination (3.472 Å), our computed $a$ (7.641 Å) and $c$ (7.532 Å) lattice constants overshoot their comparable experimental evaluations by 6.0 % and 6.8 %, respectively. The shortcoming of standard DFT functionals in describing long range van der Waals interactions most likely explains the observed overestimations in $a$ and $c$ lattice
constants, in reference to their experimental measurements. To the best of our knowledge, literature provides no values of $E^r$ and $E^{coh}$ for either of the copper bromides to compare with. Nevertheless, calculated values for these two quantities coincide with the experimental values for the two copper chlorides. For example, experimental measurements of $E^{coh}$ for CuCl and CuCl$_2$ amount to 6.18 eV and 8.29 eV, respectively, i.e., in close proximity to corresponding values for CuBr (5.46 eV) and CuBr$_2$ (7.21 eV).

Figures 2 and 3 display DOS and PDOS for bulk CuBr and CuBr$_2$, respectively. Our plotted DOS curves for bulk CuBr and CuBr$_2$ match very well other theoretically-derived corresponding curves. Starting with Figure 2a, the DOS of CuBr exhibits three valance bands. The lowest band extends from -17.4 eV to -15.6 eV and comprises mainly Br(s) orbitals. Br(p) and Cu(d) states form the middlemost band (-7.3 eV to -4.9 eV) (Figure 2b and 2c) while Cu(d) orbitals contribute predominantly to the highest band stretching from -2.4 eV and up to the Fermi level (Figure 2b). Br(s), Br(p) and Cu(d) orbitals form the observed conduction band (-2.4 eV to -5.8 eV). Clearly, DOS plots in Figure 2 indicate that bulk CuBr does not exhibit any metallic character. Previous experimental and theoretical studies have also confirmed the semiconducting nature of bulk CuBr. Our calculated direct band gap for bulk CuBr (0.98 eV) is in a relative accord with others theoretical estimations i.e. 0.42 eV$^{35}$ and 0.45 eV$^{39}$ However, all available theoretical values considerably underestimate analogous experimental measurements, viz, 3.05 eV$^{38}$ and 2.91 eV$^{40}$ In contrast, the extension of the highest valence band in bulk CuBr$_2$ (Figure 3) from -6.0 eV to 1.0 eV confirms the metallic character of bulk CuBr$_2$. Experimental and theoretical studies$^{36}$ have also asserted the metallic character of CuBr$_2$ and copper (II) halides in general. The width and the location of our calculated valance band concur with experimental data derived by photoelectron spectra.$^{37}$ Our GGA calculations (Figure 3) and LDA calculations
by Lebernegg et al.\textsuperscript{36} show that the metallicity of CuBr\textsubscript{2} stems from combination involving Cu(3d) and Br(4p) orbitals.

3.2. Geometries of CuBr and CuBr\textsubscript{2} low-index surfaces

Surface terminations of bulk CuBr\textsubscript{2} affords six distinct low-index configurations, namely, (100), (010), (001), (110), (101), and (111). The unoptimised (i.e. initial) surfaces of (010), (110) and (111) contain both Cu and Br atoms in their outermost layers. On the other hand, the initial (100), (001) and (101) surfaces may encompass either Br or Cu atoms in their topmost layers, resulting in two unequivalent low-index terminations for each surface. It follows that there are nine different initial CuBr\textsubscript{2} surfaces. In subsequent discussion, surfaces are termed based on their atomic-type terminations and orientations in their final converged structures. For example, the CuBr\textsubscript{2}(001)\textsubscript{Br} structure denotes a CuBr\textsubscript{2} surface orientated along the (001) direction, containing only Br atoms at its outermost layers. Similarly, surface terminations of the cubic CuBr unit cell produce constructions along the (010), (001) and (111) indices. The (001) configuration could be either Cu- or Br-terminated. Figure 4 depicts side and top views of CuBr surfaces whereas Figures 5 and 6 illustrate structural views for CuBr\textsubscript{2} surfaces. Table 2 and 3 provide summary of optimised geometries, and bromine to copper ratios, \( R(\text{Br}/\text{Cu}) \), for CuBr and CuBr\textsubscript{2} configurations, respectively. Table 4 accounts for differences between relaxed and ideal interlayer distances, i.e. \( \Delta d_{ij} \).

Inspection of geometries in Table 2 reveals that Cu-Br distances in CuBr surfaces depart from their corresponding bulk value slightly in the range of -1.3 % - 3.0%. The two dissimilar Cu-Br types of bonds in CuBr\textsubscript{2} constructions fall within comparable deviations in reference to their corresponding values in bulk CuBr\textsubscript{2}. Cu-Br distances in the outermost two layers are
generally shortened (~ 5.0 %) when compared with inner bonds. However, Cu-Br distances in the second layer of the CuBr(001)_{Br} structure are longer than corresponding bonds in the first layer (i.e. 2.59 Å versus 2.49 Å). Cu-Cu distances in all considered copper bromide configurations deviate marginally from their analogous values in bulk CuBr and CuBr₂. Closed-packed structures typically display rather small relaxations.\(^{41}\) Table 4 indicate that surfaces terminated initially with Cu atoms incur higher $\Delta d_{ij}$ values. Examining the $R(\text{Br/Cu})$ ratios in Tables 2 and 3, we notice that some layers comprise equal numbers of Br and Cu atoms (i.e. stoichiometric surfaces) while other exhibit either an excess of Br or Cu atoms (i.e. polar surfaces). In the next section, we will discuss further the effect of $R(\text{Br/Cu})$ ratios on thermodynamic stability of CuBr/CuBr₂ surfaces.

We are now in a position to convey some remarks with regard to the optimised geometries of CuBr and CuBr₂ surfaces:

- Overall, comparisons between geometries of bulk CuBr and CuBr₂ with optimised CuBr and CuBr₂ slabs indicate that the latter retain, to a large extent, the characteristic features of the former.
- The CuBr₂(001)_{CuBr} was truncated initially with only Cu atoms in its topmost layers, while its minimum energy structure reveals that this surface becomes terminated with both Cu and Br atoms. The first Cu-containing layer in the initial structure displays a 0.38 Å downward displacement and the second Br-containing layer experiences a 0.54 Å upward movement. The optimised structure of the CuBr₂(101)_{CuBr} also expresses a similar behaviour to that of CuBr₂(001)_{CuBr} regarding the descending of the first Cu-terminated layer. Along the same line of observation, the initial configuration of the CuBr(110)_{Br} surface contains both Cu
and Br atoms in the two topmost layers whereas the final optimised structure is truncated with only Br atoms. As Table 4 depicts, surfaces that experience downward displacement of Cu atoms are associated with negative $\Delta d_{ij}$ values. Downward displacement of the first Cu-atomic layers was also observed in CuCl$_2$ and FeCl$_2$/FeCl$_3$ surfaces.

- The side views of CuBr(001)$_{Br}$ and CuBr$_2$(001)$_{Br}$ surfaces suggest that, structural arrangements of certain CuBr surfaces are similar to those of CuBr$_2$ surfaces.

### 3.3. Electronic properties

Bader’s theory provides a reliable and robust approach to partition the continuous charge density into individual charges on separated atoms. Table 5 lists Bader’s charges on selected Br and Cu atoms belonging to their corresponding 1-3 topmost atomic layers in all CuBr and CuBr$_2$ surfaces (refer to Figures 4-6 for positions of selected atoms). Charges on surface atoms may be contrasted with analogous calculated charges on bulk atoms. Cu atoms in bulk CuBr and CuBr$_2$ hold net positive charges of 0.40 $e$ and 0.70 $e$, respectively. Br atoms in the two bulk structures are associated with negative charges of 0.40 $e$ and 0.35 $e$. It follows that Cu-Br bonds in CuBr$_2$ surfaces exhibit slightly more ionic character than corresponding bonds in structures of CuBr. The fact that copper (II) bromide is more soluble in water and other solutions than copper (I) bromide is in line with our prediction that Cu-Br bonds in the former are slightly more ionic than those in the latter. However, despite of some differences in atomic charges between CuBr and CuBr$_2$, values of charges shown in Table 5 affirm the largely covalent nature of copper bromides.

By inspection of Bader’s charges in Table 5, we make the following comments:
- Br atoms in slabs of CuBr generally exhibit more partial negative charge in reference to bulk Br atoms (i.e. -0.40 e).

- Charges on Br atoms in the topmost layers of Br-terminated surfaces remain close to their corresponding bulk values (i.e. CuBr(001)_Br and CuBr₂(001)_Br slabs). Partial positive charges on the second topmost Cu-containing layers in these Br-truncated surfaces are larger than those on other surfaces. This indicates that, the topmost Cu-Br bonds in these surfaces are more ionic than the corresponding Cu-Br bonds in other Cu- and CuBr-terminated surfaces.

- Charges on inner Cu atoms are generally very close to their analogous values in bulk CuBr and bulk CuBr₂.

- Electronegativity of Br atoms in the topmost layer of CuBr-terminated surfaces slightly overshoot respective bulk values (i.e, -0.40 e and -0.35 e).

Plausible effects of partial charges on the stability ordering of CuBr and CuBr₂ surfaces will be discussed in next section.

Figure 7 and 8 show DOS and PDOS for two selected surfaces, CuBr(111)_CuBr and CuBr₂(001)_Br. Clearly, the DOS curves in these two figures represent analogous DOS/PDOS energy band intervals and contributing orbitals shown in Figures 2 and 3 for bulk CuBr and CuBr₂. Albeit, the two upper valance bands in bulk CuBr merge to form one energy state extending from -7.5 eV to just above the Fermi level, in the CuBr(111)_CuBr surface. As evident from the occupying energy states around the Fermi level, the CuBr₂(001)_Br surface shows metallic character. To the best of our knowledge, literature provides no analogous theoretical or experimental data on DOS of CuBr and CuBr₂ surfaces.

Practically, values of $\Delta\mu_{Br}(T,P)$ may vary only between two bounded limits; i.e., Br-lean and Br-rich limits. These two boundaries denote experimentally accessible conditions of chemical potential of bromine. The Br-lean limit signifies a value of $\Delta\mu_{Br}(T,P)$ at which bulk CuBr commences to form upon the presence of a clean bulk copper in a bromine gas reservoir. The onset for decomposition of gases bromine into Br atoms marks the Br-rich limit of $\Delta\mu_{Br}(T,P)$. Well-defined limits for these two boundaries are typically$^{26,45}$ considered to be $E^f$ (Br-rich) and zero (Br-lean). Thus, according to calculated $E^f$ values in Table 1, Br-rich limits for slabs of CuBr and CuBr$_2$ are assigned values at -0.67 eV and -1.17 eV, in that order. Table 6 provides $\gamma(T,P)$ at the two $\Delta\mu_{Br}(T,P)$ limits for all CuBr and CuBr$_2$ surfaces. It must be noted that slabs of CuBr(111)$_{CuBr}$ and CuBr$_2$(101)$_{CuBr}$ are not exactly symmetric. Consequently, calculated surface energies for these two surfaces represent average values between their top and bottom terminations.

Between Br-lean and Br-rich limits, a thermodynamic equilibrium establishes. Figure 9 plots the dependence of $\gamma(T,P)$ on the gradual variations of $\Delta\mu_{Br}(T,P)$. Values of $\gamma(T,P)$ for stoichiometric terminations (i.e, $N_{Br} = N_{Cu}$ in CuBr slabs) are independent of the change in $\Delta\mu_{Br}(T,P)$. The energy phase diagram in Figure 9a infers that, the CuBr(001)$_{Br}$ dominates the stability ordering of CuBr surfaces across the entire accessible range of $\Delta\mu_{Br}(T,P)$. In practical terms, this finding indicates that, the immersion of bulk Cu in a Br$_2$ gas-phase environment leads solely to the formation a CuBr(001)$_{Br}$ phase. Experiments involving low-energy electron diffraction reported the formation of c(2 $\times$ 2) pattern, an intermediate
configuration for the formation of bulk CuBr, upon initial interaction of a Cu(100) surface with Br$_2$. In order to explain the profound thermodynamic stability of the CuBr(001)$_{\text{Br}}$ in view of the experimental results, we studied the $c(2 \times 2)$ bromine adsorption at bridge sites of a Cu(100) surface (yellow-coloured spheres denote second-layer Cu atoms):

The top view of this structure resembles the top view of the CuBr(001)$_{\text{Br}}$ structure (Figure 4). Chemisorption energy for this structure amounts to -1.76 eV. Cu-Br distances are 2.58-2.63 Å, i.e. very close to the corresponding range of Cu-Br distances for the CuBr(001)$_{\text{Br}}$ structure (Table 2). Nevertheless, we are not in a position to comment on the thermodynamic favourability of this configuration in comparison to other plausible configurations in the Br$_2$ + Cu(100) system (i.e. degree of coverages, adsorption sites, on-surface versus subsurface adsorptions). All what we can conclude here is that, the experimentally observed $c(2 \times 2)$ bromine adsorption on a Cu(100) surface represents an initial (i.e. precursor) structure for the formation of the most stable CuBr termination of CuBr(001)$_{\text{Br}}$.

Whereas the stability of the CuBr(001)$_{\text{Br}}$ structure is easily recognised among CuBr surfaces within the physically meaningful range of $\Delta \mu_p (T, P)$, the situation is rather vague in the stability phase diagram of CuBr$_2$ surfaces (Figure 10b) in which the stability lines of several configurations lay within 40.0 meV. The latter quantity most likely resides within the uncertainty limit of this type of calculations. Most notably, $\gamma(T, P)$ curves for the two stable surfaces at $\Delta \mu_p (T, P) \leq -0.75$ eV, namely, CuBr$_2$(110)$_{\text{CuBr}}$ and CuBr$_2$(101)$_{\text{CuBr}}$, are
almost indistinguishable. Likewise, for $\Delta\mu_{\text{Br}}(T, P) > -0.75$ eV, the CuBr$_2$(100)$_{\text{Br}}$ surface is marginally more stable than the other Br-terminated surface of CuBr$_2$(101)$_{\text{Br}}$. The transition in thermodynamic stability ordering from two CuBr-terminated configurations into pure Br-terminated surfaces matches the recently observed trend in CuCl$_2$ system.\textsuperscript{42} This shift in stability could be rationalised in view of the reactive nature of Cu atoms in the topmost CuBr-containing layers which tend to absorb more bromine atoms as the gaseous bromine content increases. Furthermore, our reported stability ordering implies that the topmost CuBr-bulk like structures in CuBr$_2$(110)$_{\text{CuBr}}$ and CuBr$_2$(101)$_{\text{CuBr}}$ transform into topmost CuBr$_2$-bulk like structures with the increase in concentration of gaseous bromine, which is intuitively very appealing. The observed high stability of CuBr$_2$(100)$_{\text{Br}}$ and CuBr$_2$(101)$_{\text{Br}}$ structures coincide with conclusions of several ab initio atomistic thermodynamics studies\textsuperscript{27,42,43,46,47} pointing out that surfaces covered with electro negatively charged atoms (such as Cl and O) afford the most stable configurations.

Next, we attempt to relate the predicted stability sequence with geometrical and electronic properties of surfaces. Previously discussed factor affecting ordering of thermodynamic stability include the degree of surface relaxation,\textsuperscript{48} reduction in charge at topmost layers\textsuperscript{47} and the overall polarity of the slab.\textsuperscript{45} The comparable relaxations of layers among CuBr surfaces (Table 4) suggest that deviation of surface geometries from bulk positions is not the driving factor behind the noticeable stability of the CuBr(001)$_{\text{Br}}$ surface. Furthermore, despite its very minimal inter layers relaxation, the CuBr$_2$(100)$_{\text{Br}}$ slab holds more stability than the CuBr$_2$(100)$_{\text{Cu}}$ surface which is associated with a larger relaxation. The fact that Cu atoms in the second Cu-containing layers in CuBr(001)$_{\text{Br}}$ and CuBr$_2$(100)$_{\text{Br}}$ carry slightly more positive charges than in other slabs may contribute to the profound stability of these Br-covered surfaces. Contrasting the $R$ ratios in Table 3 with the stability lines in Figure 10
leads us to conclude that polarity does not represent a governing stability factor. Regal et al.\textsuperscript{45} reached the same conclusion in their analysis of the PdO surfaces. The realisation that the CuBr(001)\textsubscript{Br} represents a Br-rich surface while the CuBr\textsubscript{2}(110)\textsubscript{CuBr} constitutes a Cu-rich surface overrules the elemental composition (and hence the $R$ ratios) as a chief stability-determining factor.

In a nutshell, thermodynamic stability ordering is most likely to be derived by incremental contributions from combined factors and not driven by a single factor. Surfaces covered with electronegative-charged atoms if accompanied with significant relaxations tend to be more stable.

Finally, Figure 10 depicts the change in Wulff construction for CuBr and CuBr\textsubscript{2} single crystal based on the energy phase diagram presented in Figure 9. As expected, the area of the CuBr\textsuperscript{r} facet that is covered with the CuBr(001)\textsubscript{Br} phase increases with the bromine chemical potential. The shape of the CuBr\textsubscript{2} nanoparticle reflects the very comparable stability lines of many CuBr\textsubscript{2} phases.

4. Conclusions and future directions

In spite of prominent industrial and environmental applications, little detailed information is available on bulk and surfaces of copper bromides. We compared geometries and electronic charges of copper bromide surfaces with corresponding values in their bulk structures. Calculated lattice constants of the latter were found to be in relative agreement with limited
experimental measurements. Plots of DOS for a CuBr$_2$ surfaces confirm its metallic characters whereas the PDOS of a CuBr surface indicates that it is a semiconductor. Inner Cu and Br atoms in surfaces were found to bear charges similar to those of bulk configurations. The transition in stability of CuBr$_2$ surfaces from CuBr-terminated layers to Br-covered layers implies a shift from CuBr-bulk like structures to CuBr$_2$-bulk like structures with the increase in the concentration of gaseous bromine.

Finally, we want to highlight few possible implications for future research directions based on the results presented in this study. While we have made attempts to elucidate factors governing thermodynamic stability of CuBr and CuBr$_2$ surfaces, several other aspects warrant further investigations. We have limited our analysis to perfect slabs, leaving the presence of surface defects on the stability orderings for further investigation. Furthermore, obtaining optimised geometries for copper bromide surfaces may pave the way to address their chief catalytic role in bromination of aromatic compounds.

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References


Table 1. Calculated few properties of bulk CuBr and CuBr₂.

<table>
<thead>
<tr>
<th></th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>β/°</th>
<th>E/ eV</th>
<th>E°coh/ eV</th>
</tr>
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<tbody>
<tr>
<td>CuBr</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>This work</td>
<td>5.796</td>
<td>5.796</td>
<td>5.796</td>
<td>-0.67</td>
<td>-5.46</td>
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</tr>
<tr>
<td>Expt⁴³</td>
<td>5.696</td>
<td>5.696</td>
<td>5.696</td>
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<tr>
<td>CuBr₂</td>
<td></td>
<td></td>
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</tr>
<tr>
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<td>7.532</td>
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<td>-7.21</td>
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<td>3.472</td>
<td>7.048</td>
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Table 2. Summary of optimised geometries for CuBr configurations. Distances are in Å.

<table>
<thead>
<tr>
<th>Surface</th>
<th>R (Br/Cu)</th>
<th>Cu-Br</th>
<th>Cu-Cu</th>
<th>Comments (distances in Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuBr(001)_Br</td>
<td>40/36</td>
<td>2.35-2.59</td>
<td>3.89</td>
<td>The range in Cu-Br bonds refer to surface Cu-Br bond (2.35) and a second-layer Cu-Br bond (2.59) where all inner Cu-Br bonds are 2.49.</td>
</tr>
<tr>
<td>CuBr(001)_Cu</td>
<td>32/36</td>
<td>2.40-2.45</td>
<td>3.89</td>
<td>Surface C-Br bonds are 2.40.</td>
</tr>
<tr>
<td>CuBr(110)_Br</td>
<td>44/44</td>
<td>2.39-2.44</td>
<td>3.89</td>
<td>Surface C-Br bonds are 2.39.</td>
</tr>
<tr>
<td>CuBr(111)_CuBr</td>
<td>52/52</td>
<td>2.33-2.42</td>
<td>3.83</td>
<td>All surface Cu-Br bonds are 2.33.</td>
</tr>
</tbody>
</table>
Table 3. Summary of optimised geometries for CuBr$_2$ configurations. Distances are in Å.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$R$ (Br/Cu)</th>
<th>Short Cu-Br</th>
<th>Long Cu-Br</th>
<th>Cu-Cu</th>
<th>Comments (distances in Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuBr$<em>2$(100)$</em>{Br}$</td>
<td>38/19</td>
<td>2.39-2.58</td>
<td>3.25</td>
<td>3.48</td>
<td>Surface Cu-Br bonds are 2.39 and inner bonds are 2.41.</td>
</tr>
<tr>
<td>CuBr$<em>2$(100)$</em>{Cu}$</td>
<td>31/19</td>
<td>2.32-2.42</td>
<td>3.13</td>
<td>3.27</td>
<td>Surface Cu-Br bonds are 2.32.</td>
</tr>
<tr>
<td>CuBr$<em>2$(010)$</em>{CuBr}$</td>
<td>34/17</td>
<td>2.41-2.46</td>
<td>3.12</td>
<td>3.49</td>
<td>Surface Cu-Br bonds are 2.41.</td>
</tr>
<tr>
<td>CuBr$<em>2$(001)$</em>{Br}$</td>
<td>56/28</td>
<td>2.42-2.44</td>
<td>3.23</td>
<td>3.48</td>
<td>Surface Cu-Br bonds are equal to inner Cu-Br bonds.</td>
</tr>
<tr>
<td>CuBr$<em>2$(001)$</em>{CuBr}$</td>
<td>48/28</td>
<td>2.25-2.44</td>
<td>3.11</td>
<td>3.48</td>
<td>Surface Cu-Br bonds are 2.25.</td>
</tr>
<tr>
<td>CuBr$<em>2$(110)$</em>{CuBr}$</td>
<td>16/10</td>
<td>2.39-2.43</td>
<td>3.28</td>
<td>3.29-3.57</td>
<td>Surface Cu-Br bonds are 2.39 and inner bonds are 2.41.</td>
</tr>
<tr>
<td>CuBr$<em>2$(101)$</em>{Br}$</td>
<td>38/19</td>
<td>2.42-2.45</td>
<td>3.32</td>
<td>3.48</td>
<td>Surface Cu-Br bonds are 2.42.</td>
</tr>
<tr>
<td>CuBr$<em>2$(101)$</em>{CuBr}$</td>
<td>38/19</td>
<td>2.34-2.42</td>
<td>3.32</td>
<td>3.47</td>
<td>Surface Cu-Br bonds are 2.34.</td>
</tr>
<tr>
<td>CuBr$<em>2$(111)$</em>{CuBr}$</td>
<td>38/19</td>
<td>2.43-2.46</td>
<td>3.12</td>
<td>3.50-3.56</td>
<td>Surface Cu-Br bonds are 2.43.</td>
</tr>
</tbody>
</table>
Table 4. Differences between relaxed and ideal interlayer distances ($\Delta d_{ij}$). Values are in Å.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta d_{12}$</th>
<th>$\Delta d_{23}$</th>
<th>$\Delta d_{34}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuBr(001)$_{Br}$</td>
<td>0.39</td>
<td>0.27</td>
<td>0.30</td>
</tr>
<tr>
<td>CuBr(001)$_{Cu}$</td>
<td>0.21</td>
<td>0.11</td>
<td>0.10</td>
</tr>
<tr>
<td>CuBr(110)$_{CuBr}$</td>
<td>-0.96</td>
<td>0.18</td>
<td>0.29</td>
</tr>
<tr>
<td>CuBr(111)$_{CuBr}$</td>
<td>-1.74</td>
<td>0.34</td>
<td>0.34</td>
</tr>
<tr>
<td>CuBr$<em>2$(100)$</em>{Br}$</td>
<td>0.06</td>
<td>0.04</td>
<td>0.08</td>
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<tr>
<td>CuBr$<em>2$(100)$</em>{Cu}$</td>
<td>0.01</td>
<td>0.78</td>
<td>0.24</td>
</tr>
<tr>
<td>CuBr$<em>2$(010)$</em>{CuBr}$</td>
<td>0.36</td>
<td>-0.22</td>
<td>0.11</td>
</tr>
<tr>
<td>CuBr$<em>2$(001)$</em>{Br}$</td>
<td>0.02</td>
<td>0.04</td>
<td>-0.02</td>
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<tr>
<td>CuBr$<em>2$(001)$</em>{CuBr}$</td>
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<td>0.48</td>
<td>0.07</td>
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<tr>
<td>CuBr$<em>2$(101)$</em>{Br}$</td>
<td>0.00</td>
<td>0.11</td>
<td>0.01</td>
</tr>
<tr>
<td>CuBr$<em>2$(110)$</em>{CuBr}$</td>
<td>-0.19</td>
<td>-0.16</td>
<td>0.30</td>
</tr>
<tr>
<td>CuBr$<em>2$(111)$</em>{CuBr}$</td>
<td>0.28</td>
<td>-0.52</td>
<td>0.09</td>
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Table 5. Calculated Bader’s charges on selected Cu and Br atoms. Numbering refer to atoms in first, second and third layers. Numbers are in the unit of $e$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Cu&lt;sub&gt;1&lt;/sub&gt;</th>
<th>Cu&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Cu&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Br&lt;sub&gt;1&lt;/sub&gt;</th>
<th>Br&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Br&lt;sub&gt;3&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuBr(001)_Br</td>
<td>0.56</td>
<td>0.49</td>
<td>0.51</td>
<td>-0.44</td>
<td>-0.44</td>
<td>-0.47</td>
</tr>
<tr>
<td>CuBr(001)_Cu</td>
<td>0.27</td>
<td>0.48</td>
<td>0.48</td>
<td>-0.42</td>
<td>-0.49</td>
<td>-0.49</td>
</tr>
<tr>
<td>CuBr(110)_CuBr</td>
<td>0.42</td>
<td>0.48</td>
<td>0.50</td>
<td>-0.52</td>
<td>-0.42</td>
<td>-0.49</td>
</tr>
<tr>
<td>CuBr(111)_CuBr</td>
<td>0.32</td>
<td>0.48</td>
<td>0.50</td>
<td>-0.41</td>
<td>-0.42</td>
<td>-0.45</td>
</tr>
<tr>
<td>CuBr&lt;sub&gt;2&lt;/sub&gt;(100)_Br</td>
<td>0.67</td>
<td>0.67</td>
<td>0.67</td>
<td>-0.30</td>
<td>-0.30</td>
<td>-0.30</td>
</tr>
<tr>
<td>CuBr&lt;sub&gt;2&lt;/sub&gt;(100)_Cu</td>
<td>0.63</td>
<td>0.66</td>
<td>0.65</td>
<td>-0.42</td>
<td>-0.40</td>
<td>-0.40</td>
</tr>
<tr>
<td>CuBr&lt;sub&gt;2&lt;/sub&gt;(010)_CuBr</td>
<td>0.67</td>
<td>0.69</td>
<td>0.69</td>
<td>-0.38</td>
<td>-0.35</td>
<td>-0.35</td>
</tr>
<tr>
<td>CuBr&lt;sub&gt;2&lt;/sub&gt;(001)_Br</td>
<td>0.72</td>
<td>0.72</td>
<td>0.72</td>
<td>-0.36</td>
<td>-0.36</td>
<td>-0.36</td>
</tr>
<tr>
<td>CuBr&lt;sub&gt;2&lt;/sub&gt;(001)_CuBr</td>
<td>0.50</td>
<td>0.70</td>
<td>0.70</td>
<td>-0.45</td>
<td>-0.39</td>
<td>-0.35</td>
</tr>
<tr>
<td>CuBr&lt;sub&gt;2&lt;/sub&gt;(110)_CuBr</td>
<td>0.56</td>
<td>0.60</td>
<td>0.60</td>
<td>-0.46</td>
<td>-0.44</td>
<td>-0.44</td>
</tr>
<tr>
<td>CuBr&lt;sub&gt;2&lt;/sub&gt;(101)_Br</td>
<td>0.65</td>
<td>0.66</td>
<td>0.67</td>
<td>-0.35</td>
<td>-0.33</td>
<td>-0.30</td>
</tr>
<tr>
<td>CuBr&lt;sub&gt;2&lt;/sub&gt;(101)_CuBr</td>
<td>0.67</td>
<td>0.54</td>
<td>0.67</td>
<td>-0.44</td>
<td>-0.33</td>
<td>-0.33</td>
</tr>
<tr>
<td>CuBr&lt;sub&gt;2&lt;/sub&gt;(111)_CuBr</td>
<td>0.68</td>
<td>0.70</td>
<td>0.70</td>
<td>-0.36</td>
<td>-0.37</td>
<td>-0.32</td>
</tr>
</tbody>
</table>
Table 6. Values of $\gamma(T, P)$ for all surfaces at Br-lean and Br-lean limits. All values are in meV/Å$^2$.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Br-lean</th>
<th>Br-rich</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuBr(001)_Br</td>
<td>-16.4</td>
<td>-36.2</td>
</tr>
<tr>
<td>CuBr(001)_Cu</td>
<td>276.1</td>
<td>296.0</td>
</tr>
<tr>
<td>CuBr(110)_CuBr</td>
<td>-7.3</td>
<td>-7.3</td>
</tr>
<tr>
<td>CuBr(111)_CuBr</td>
<td>7.3</td>
<td>7.3</td>
</tr>
<tr>
<td>CuBr$_2$(100)_Br</td>
<td>-33.1</td>
<td>-33.1</td>
</tr>
<tr>
<td>CuBr$_2$(100)_Cu</td>
<td>-41.3</td>
<td>171.3</td>
</tr>
<tr>
<td>CuBr$_2$(010)_CuBr</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>CuBr$_2$(001)_Br</td>
<td>-15.5</td>
<td>-15.5</td>
</tr>
<tr>
<td>CuBr$_2$(001)_CuBr</td>
<td>-31.5</td>
<td>176.1</td>
</tr>
<tr>
<td>CuBr$_2$(110)_CuBr</td>
<td>-61.6</td>
<td>144.3</td>
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<tr>
<td>CuBr$_2$(101)_Br</td>
<td>-54.7</td>
<td>157.8</td>
</tr>
<tr>
<td>CuBr$_2$(101)_CuBr</td>
<td>-27.5</td>
<td>-27.5</td>
</tr>
<tr>
<td>CuBr$_2$(111)_CuBr</td>
<td>-1.8</td>
<td>-1.8</td>
</tr>
</tbody>
</table>
Figure 1. Unit cells of bulk CuBr (a) and CuBr$_2$ (b). Dark (blue-coloured) spheres denote bromine atoms.
Figure 2. Total and partial density of states for bulk CuBr.
Figure 3. Total and partial density of states for bulk CuBr$_2$. 

(a) Total

(b) Cu

(c) Br
Figure 4. Optimised geometries of CuBr slabs shown as 3 by 3 cells. Dark larger (blue-coloured) spheres denote bromine atoms.
Figure 5. Optimised geometries of CuBr$_2$ slabs shown as 3 by 3 cells. Dark larger (blue-coloured) spheres denote bromine atoms. Structure of the CuBr$_2$(100)$_\text{Cu}$ is similar to that of CuBr$_2$(100)$_\text{Br}$ with the deletion of Br atoms in two outermost layers.
Figure 6. Optimised geometries of CuBr$_2$ slabs shown as 3 by 3 cells. Dark (blue-coloured) spheres denote bromine atoms.
Figure 7. Total and partial density of states for CuBr(111)_CuBr surface.
Figure 8. Total and partial density of states for CuBr$_2$(001)$_{\text{Br}}$ surface.
Figure 9. Stability phase diagram of CuBr (a) and CuBr$_2$ (b) surfaces.
**Figure 10.** Change in the Wulff constructions of CuBr and CuBr$_2$ nanoparticles with variations in bromine chemical potentials.