# First principles study of halogens adsorption on intermetallic surfaces

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ABSTRACT

Halides are often present at electrochemical environment, they can directly influence the electrode potential or zero charge potential through the induced work-function change. In this work, we focused in particular on the halogen-induced work function change as a function of the coverage of fluorine, chlorine, bromine and iodine on $Al_2Au$ and $Al_2Pt$ (110) surfaces. Results show that the real relation between work function change and dipole moment change for halogens adsorption on intermetallic surfaces is just a common linear relationship rather than a directly proportion. Besides, the different slopes between fitted lines and the theoretical slope employed in pure metal surfaces demonstrating that the halogens adsorption on intermetallic surfaces are more complicated. We also present a weight parameter $\beta$ to describe different factors effect on work function shift and finally qualify which factor dominates the shift direction.

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## 1. Introduction

Over the past few years, binary intermetallic compounds that crystallize in the cubic fluorite structure ($CaF_2$) have received considerable attentions [1–6]; $Al_2Au$ and $Al_2Pt$ are such compounds of both technological and scientific importance. The former has potential applications as a selective solar absorber [7] and the latter was proposed to be used as a thermodynamically stable conducting contact to GaAs [8]. Moreover, they can be used to study the dealloying phenomenon, since the component elements Al and Au or Pt have large standard potential difference [9]. In particular, $Al_2Au$ is an excellent choice as precursor for the fabrication of gold catalysts with a tailored pore size [10–16]. In addition to the bulk studies, the $Al_2Au$ phase has been produced in the form of thin films with various possible applications in mind, ranging from decorative and spectrally selective coatings [2] to hard coatings on cutting tools [17,18], and even as a material for transparent electrodes [19].

The presence of specifically adsorbed anions can significantly influence the electrochemical behaviors of a metal or alloy surface which is of major relevance for electro-catalysis reaction [20–23], galvanic deposition [24,25], and etching [26,27] and corrosion protection [28–36]. Halide ions are the most simple and prototype of anions and ubiquitous in natural and technological environments, their adsorption on metal single crystal surfaces has been

investigated in great detail but very scarce research for alloy surfaces especially intermetallic surfaces [37]. Sellers et al. [38] reported that a simple thermodynamic cycle can be used to convert the binding energy of adsorbed halogen to the binding energy of halide ion and vice versa. Besides, the trends in binding energies of halides and halogens are often found to be identical [39]. Doll et al. [40] studied the adsorption of chlorine on the Ag (111) surface with full potential gradient corrected density functional calculations. Based on density of states analysis, they found the Cl–Ag interaction to be more consistent with an ionic rather than covalent bonding. Duan et al. [41–43] investigated the interaction of fluorine, chlorine and bromine with Mg (0001) surface for different coverages. A systematic study of the structure and bonding of halogens on low-index transition metal surfaces was done by Migani and Illas [44]. The authors demonstrated that higher work function surfaces are associated with more covalent bonding, while established periodic trends in bond ionicities and metal-halogen vibrational frequencies indicate that metal-halogen bonding in vacuum interrelates with metal electrode-halogen bonding in electrochemical environment. Therefore, we prefer to study the halogen adsorption case instead of halide ion adsorption, since such a charge-neutral situation may be conveniently linked to the scale of electrochemical potentials by means of the potential of zero charge [39].

The surface work function is a fundamental routinely measured property in electrochemistry, as Roman et al. have shown that adsorbates can directly influence the electrode potential or zero charge potential through the induced work-function change

[22]. The dipole moment change is generally used to interpret or evaluate the corresponding work function change induced by adsorbates. Although this method is widely adopted by other researchers to study the adsorption systems [31,45–50], it should be noted that the method is based on the assumption of a relation between work function change and the dipole moment change. Fortunately, Leung et al. [51] demonstrated the simple relationship between surface dipole moment density and work function change within the framework of local-density formalism for a large number of elements adsorbed on various orientations of W substrates. Roman et al. [52] verified that the relationship is also correct for halogens adsorption on Pt (111) surface over a variety of coverages within the framework of generalized gradient approximation. However, to our knowledge, it is still lack of innovative investigation of halogens on intermetallic surfaces to prove the robustness of the linear relationship so far. Theoretical studies concerning the surface work function changes of Al$_2$Au and Al$_2$Pt in halides environment are needed due to the interest in employing these systems to study the anion species and concentration dependent dealloying of Al$_2$Au and Al$_2$Pt and as a template to fabricate nanoporous Au and Pt. In this paper, we focused in particular on the halogen-induced work function change as a function of the coverage of fluorine, chlorine, bromine and iodine for the (110) surface of these two intermetallic materials.

## 2. Computational methods

For the following calculations, the density functional theory (DFT) program Vienna Ab Initio Simulation Package (VASP) is used [53]. The exchange and correlation energy adopts the generalized gradient approximation (GGA) with the PBE functional which developed by Perdew et al. [54]. This functional is so widely used because it has been shown to give reliable results in terms of atomization energy [55], chemisorption energies [56], work function changes [52,57], and good estimates of bulk properties of metals [58].

To describe the ionic cores of the atoms, we use the projector augmented wave potentials (PAW) constructed by Kresse and Joubert [59]. The energy cutoff for plane wave basis set is up to 500 eV, and a Monkhorst–Pack k-grid was adopted for all the calculations. For k-space integration, the temperature smearing method of Methfessel–Paxton [60] is used for relaxation calculation. For bulk calculation, a unit cell of twelve atoms with a k-mesh of 5 × 5 ×5 is adopted for Al$_2$Au and Al$_2$Pt. The atoms are fully relaxed to find out the optimized lattice constant corresponding to the lowest total energy, and the optimized lattice constants from the bulk calculation are used for the corresponding surface calculations.

For the surface calculation, only three low-index orientations of (001), (110), and (111) are selected in the present study. Specifically, a $\sqrt{2} \times \sqrt{2}$ surface unit cell is used for the (001) Al$_2$Au and Al$_2$Pt surfaces, as well as for the (111) surfaces, while a $2 \times \sqrt{2}$ surface unit cell is chosen for the (110) surface of Al$_2$Au and Al$_2$Pt. For the k-points, the grids of $4 \times 4 \times 1$ is adopted for all (001) and (111) surfaces, while $3 \times 4 \times 1$ for all (110) surfaces. The criteria for ionic and electronic convergence were set to $10^{-6}$ and $10^{-7}$ eV respectively for the difference between successive optimization steps. The Bader charge analysis is done using algorithms developed from the Henkelman group for the VASP code [61,62].

The work function is obtained from the difference between the Fermi energy and the average local potential of electrons in the vacuum, where the potential does not change anymore with increasing distance from the surface. Dipole corrections were applied in the surface perpendicular direction to prevent interactions between periodic surface slabs.

The halogens adsorption energies are calculated according to the following equation:

$$E_{ads} = \frac{1}{N}(E_{tot} - E_{clean} - NE_{halogen}) \tag{1}$$

Here $N$ is the number of halogen atoms adsorbed on the surface, $E_{tot}$ is the total energy of the (110) surface with adsorbed halogen atoms, $E_{clean}$ is the energy of the clean relaxed (110) surface, $E_{halogen}$ is the energy of a halogen atom in the vacuum obtained through a broken symmetry spin-polarized calculation of a single halogen atom in a $15 \times 15 \times 15$ Å cubic box.

## 3. Results and discussion

### 3.1. Bulk characteristics of Al$_2$Au and Al$_2$Pt

The Al$_2$Au and Al$_2$Pt crystals have the CaF$_2$-type face-centered cubic (Fcc) structure with space group of Fm-3m, as Fig. 1 shows that Al atoms occupy the vertex and face centered sites while Au or Pt occupy the 8c (0.25, 0.25, 0.25) site. The lattice parameters optimized for the bulk cases yield 6.065 (6.00)[3] and 5.945 (5.926) Å [63] for Al$_2$Au and Al$_2$Pt, respectively, with the experimental data given in parentheses. It is seen that the results of DFT calculations are very consistent with the corresponding experimental data. Thus, the paw pseudopotential incorporated with GGA-PBE exchange correlation functional is very suited for these two intermetallic compound materials. Bader charge analysis shows that Au and Pt atoms gain 3.36 and 3.63 electrons in Al$_2$Au and Al$_2$Pt crystals respectively, such large electrons transfer indicating that a high ionic bonding strength exists in the crystal.

### 3.2. Surface properties of Al$_2$Au and Al$_2$Pt

This section briefly summarizes the main results concerning the clean surfaces. The reason to include the results of the clean surfaces is to be able to discuss the effect of halogens adsorption on their electronic structure. Therefore, a minimum description of the clean surfaces, using the same theoretical approach, is a necessary step.

Here, three prototypical low Millar index planes are selected to study on their surface properties. From Table 1, it is seen that (110) surface has the largest work function for both Al$_2$Au and Al$_2$Pt. For
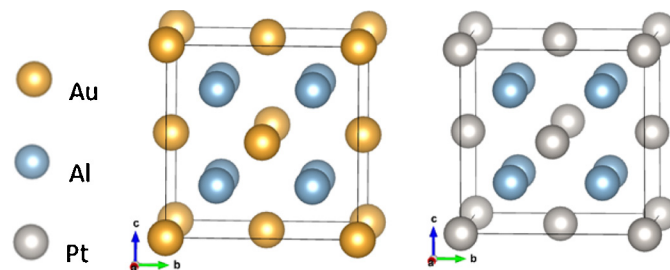


**Fig. 1.** Schematic drawing of the Al$_2$Au (left) and Al$_2$Pt (right) crystal structure.

**Table 1**
Calculated values for interlayer relaxations of the two topmost layers relative to the bulk interlayer spacing ($\delta_{12}$ and $\delta_{23}$ are in %), and the work function (eV) for different surface terminations of Al$_2$Au and Al$_2$Pt (results of the Al$_2$Pt surfaces are in the bracket).

| Surface | $\delta_{12}$ | $\delta_{23}$ | Work function |
|---|---|---|---|
| 001-Al | 0.66 (−9.40) | −1.32 (5.37) | 4.37 (4.03) |
| 001-Au (Pt) | −11.18 (−11.41) | −0.66 (−2.01) | 4.26 (4.43) |
| 110 | **−2.34 (−3.33)** | **0.93 (−0.95)** | **4.55 (4.51)** |
| 111-Al | −18.18 (−26.74) | −1.14 (−2.33) | 4.33 (4.23) |
| 111-Al$_2$ | −13.71 (−5.81) | 25 (2.33) | 4.48 (4.36) |
| 111-Au (Pt) | −19.32 (−24.42) | 4 (2.33) | 4.50 (4.48) |