Electronic Structures and Stability of Ag-In-Ca Surfaces

K. Nozawa\(^1\) and Y. Ishii\(^2\)

\(^1\)Graduate School of Materials Science, University of Hyogo, Hyogo 678-1297, Japan
\(^2\)Department of Physics, Chuo University, Tokyo 112-8551, Japan

E-mail: ishii@phys.chuo-u.ac.jp

Abstract. Surface properties and stability of quasicrystal-related complex metallic compounds Ag-In-Ca has been studied theoretically. Optimal structures of surface is obtained by relaxing the atoms in a slab to their force-free positions by the first-principles method. It is found that, after relaxation, In is at topmost position near the vacuum, Ag intrudes into the bulk and Ca is located at intermediate layers between In and Ag. To simulate STM images for the slab model, we calculate the charge distribution constructed from the electronic states in an appropriate energy range. We find that bright contrast is observed on different subsets of the In sites on surface for the charge distributions calculated from occupied and unoccupied states. Roles of the low-lying unoccupied Ca-3d states and the sp-d hybridization on surface electronic structures are discussed.

1. Introduction
Quasicrystals (QCs) are long-range ordered materials with rotational symmetry incompatible with translational one. The Fermi energy of QC-related compounds is usually located at a pseudogap in the electronic density of states and hence minimizing the band energy [1]. Such characteristic electronic structures should affect chemical properties of QC surfaces. Extensive studies on clean surfaces of Al-based QCs have shown that Al-rich surfaces are more stable than those with higher concentration of transition elements [2]. This seems reasonable if we assume that surface dangling bonds associated with transition d-states cost larger energy although the dangling bond picture is not so obvious for intermetallic compounds. One may interpret stability of the Al-rich surface as a consequence of the sp-d hybridization, which is considered important for the pseudogap formation. To understand a role of the sp-d hybridization on surface properties, it is particularly of interest to study how the selectivity and surface properties are modified for a family of Cd-based QCs [3], for which the sp-d hybridization is again considered to play an essential role [4]. In this paper, we shall investigate electronic structures of a slab model for an approximant of Cd-based QCs. Since experimental data are not available for surface of Cd-based compounds, we study electronic structures of a slab of Ag-In-Ca cubic approximant.

In the next section, we explain a slab model studied here and calculation method. In section 3, we calculate charge density distributions simulating STM images for relaxed surface and discuss possibility obtaining different STM images by changing sample bias voltage. Roles of the low-lying unoccupied Ca-3d states and the sp-d hybridization on surface electronic structures will be discussed.
2. Models and Calculation

A cubic approximant of Cd-based QCs is found in many systems such as Cd-Yb [5], Cd-Ca [6], Zn-Sc [7], Ag-In-Yb [8], Cu-Al-Sc [9] and so on. Structure of the cubic approximant is composed of icosahedral clusters on a vertex and a body-center of a cubic unit cell [3]. The core of the cluster is an atomic shell of non-icosahedral symmetry, presumably of tetrahedral shape. The second and third atomic shells are a dodecahedron of 20 atoms and an icosahedron of 12 atoms, respectively. The fourth shell is an icosidodecahedron obtained by placing 30 atoms on the edge of the third shell. A few more atoms are placed between the clusters and can be interpreted as forming a triacontahedral fifth shell interpenetrating with the neighbouring cluster [10].

Gómez has studied chemical ordering in Ag-In-Yb cubic approximant [8]. Alloy composition of the sample is Ag$_{39}$In$_{47}$Yb$_{14}$. The innermost core and the fourth shell consist of In atoms whereas the second one consists of mainly Ag. The third shell is occupied by Yb atoms as in a case of Cd-Yb and others. Here we note that the In-rich composition leads to the valence electron density (the number of valence electrons per atom) $e/a \approx 2.1$. For ternary systems with trivalent Sc such as Cu-Al-Sc, the monovalent Cu-rich composition is reported and again $e/a \approx 2.1$ is realized [9]. It may be reasonable to assume that the innermost tetrahedral core consists of Cu in this case.

We assume a chemically ordered structural model for the cubic approximant according to Gómez’s observation. Starting from atomic positions for cubic Cd$_6$Ca, we relaxed the atoms to their optimal positions under symmetry constraint that the space group is $I\bar{2}3$. A bulk model obtained here is used for constructing a slab model. A lattice constant $a$ is chosen to be 15.4118 Å as reported for Ag-In-Yb by Gómez [8].

Five-fold surface of icosahedral Ag-In-Yb has been studied by Sharma and co-workers [11]. Comparing the scanning tunneling microscope (STM) images with the structural model by Takakura et al. [10], they concluded that observed wide terraces are Yb-rich flat surfaces with high atomic density. For the two-fold (001) surface of the cubic approximant, a flat plane intersecting the cluster center is one with high atomic density. A slab model is constructed by terminating the bulk structure at a flat (001) plane intersecting the cluster center. Thickness of the slab is the same as the lattice constant of the cubic approximant and the slab is separated by a vacuum layer with the same thickness as the slab. In lateral direction, we assume the same periodicity as the cubic approximant. So size of the unit cell for calculation is $a \times a \times 2a$ with $a$ being a lattice constant of cubic approximant. The slab is in a range of $|z| \leq 0.25$ and the total number of atoms in the cell is about 190.

The cluster centers in the present slab model are at $(x, y, z) = (0, 0, \pm 0.25)$ and $(0.5, 0.5, 0.0)$. Since the atoms in the tetrahedral core are not on the flat surface intersecting the cluster center, we have some ambiguity about how to construct flat surface models. In this paper, we shall investigate three models with and without the tetrahedral core at surface: Model A has no tetrahedral core at the cluster center and hence a large hole there. Model B1 has In$_4$ tetrahedron at the cluster center at surface and the In$_4$ tetrahedron at surface is replaced by Ag$_4$ in model B2.

Electronic structure calculations and structural relaxation have been done with the ab-initio total-energy and molecular-dynamics program VASP (Vienna Ab-initio Simulation Package) [12, 13] with the projected-augmented wave (PAW) method [14]. Calculations are based on the local density approximation (LDA) in the density-functional theory. The wave functions are expanded with a plane-wave basis set up to a kinetic energy cut-off of 250 eV. The Brillouin zone is sampled with a single $k$-point (the $\Gamma$ point).

Electronic structure calculations within the density-functional theory give a narrow 4f band of Yb at 0.1-0.2 eV below the Fermi energy $E_F$ [4]. The position of the 4f band is, however, not accurate and, in fact, the photoemission experiments show that it is deeper than the calculated position [15]. This is due to well-known self-interaction error in the LDA [16], which
is considerably large for localized 4f states. To avoid such subtle aspects of the 4f states, we shall study here ternary Ag-In-Ca slab models because Ca, which has no f-states near the Fermi energy, is chemically similar to Yb.

3. Results and Discussions
The slab models are constructed by terminating the bulk structure at a flat (001) plane intersecting the cluster center. To obtain optimal structures of surface, we relax the atoms to their force-free positions. Atoms in a thin layer near the surface (up to 1.5 Å in depth) are considered for relaxation and those atoms outside of this layer are fixed to avoid unphysical deformation of bulk layers. We have checked, however, that general trends discussed below are not essentially changed if we consider more atoms for relaxation. Atomic positions after relaxation are shown in Fig.1 where Ag, In and Ca are represented in red, green and blue, respectively. Although the unrelaxed surface is flat except for the tetrahedral cluster, small corrugation is observed for the relaxed surface. If we look more carefully, we can see general trends that In is at topmost position near the vacuum, Ag intrudes into the bulk and Ca is located at intermediate layers between In and Ag.

Figure 1. Atomic positions after structural relaxation seen from (001) (top) and (010) (middle) directions. Atomic positions for the unrelaxed slab is shown in a bottom panel of (b). Ag, In and Ca are represented in red, green and blue, respectively. Atoms shown in light color (green or red) in (b) and (c) are those in the tetrahedral clusters at the surface.

The tetrahedral clusters at the surface in models B1 and B2, which are shown in light green and light red in Fig.1, are deformed significantly. The tetrahedral cluster protrudes slightly to the vacuum in the unrelaxed slab model but, after relaxation, the tetrahedron is entirely below the topmost In site. The Ag$_4$ tetrahedron is deformed and intrudes into the bulk more than the In$_4$. This is consistent with the general trends mentioned above. Those In atoms on surface
indicated by arrows in Fig. 1 are also significantly displaced in the models B1 and B2. Because of slightly larger atomic radius for Ag, the intruding Ag$_4$ cluster causes larger displacements of atoms in the surface layer.

We compare total energies of the slab models in Table 1. Here the total energy is defined as difference from that for isolated atoms. Total energies for the unrelaxed B1 and B2 are lower than that for the model A by 30 eV. In the models B1 and B2, two tetrahedral clusters (one cluster on each side of the slab) are added to the model A. Total energies of regular tetrahedral In$_4$ and Ag$_4$ clusters with the same size as that in the bulk model are calculated as -5.9 and -4.7 eV, respectively. So bonding of the tetrahedral clusters onto the surface yields considerable stabilization. After the relaxation, total energies of the models B1 and B2 are reduced more than the model A. This implies that deformation around the tetrahedral core contributes to stabilize the surface. The Ag$_4$ cluster in the model B2 is deformed more than the In$_4$ in the model B1 and hence larger reduction of the total energy in the model B2. Since the Brillouin zone sampling in the present calculation is done at a single $k$-point, the total energies may not be very accurate. So it would not be safe to discuss relative stability of the models B1 and B2. But we may conclude that the flat surface missing the tetrahedral core at the cluster center is less stable than that with the significantly deformed tetrahedral core.

### Table 1. Total energies of the slab models in eV. $\Delta E$ is reduction of the total energy after relaxation.

|                | model A | model B1 | model B2 |
|----------------|---------|----------|----------|
| unrelaxed      | -618.4  | -650.3   | -648.0   |
| relaxed        | -622.1  | -655.4   | -654.4   |
| $\Delta E$     | -3.7    | -5.1     | -6.4     |

To simulate STM images for the slab model, we calculate the surface local density of states, which is the charge distribution constructed from the electronic states in an appropriate energy range, at constant height [17]. In STM experiments, electrons tunnel from occupied states of a sample to unoccupied states of a tip with negative sample bias voltage $V_b < 0$. To simulate STM images for negative bias $V_b < 0$, the charge distribution is calculated from the occupied states in the energy window $E_F - |V_b| < \epsilon < E_F$. For positive bias $V_b > 0$, the charge distribution is calculated from the unoccupied states in the energy window $E_F < \epsilon < E_F + |V_b|$. The charge distribution calculated from the electronic states in a particular energy range is also of interest because the states near the Fermi energy are affected by surface formation and relaxation.

In Fig. 2, we show the charge distribution on a plane parallel to the surface at $z = 0.3$, which is about 1.4 Å above the topmost atoms. The charge distribution is shown in a 2x2 cell with atoms on the surface layer in a single unit cell. The charge distribution in Fig. 2 is calculated from the occupied states within 1 eV below $E_F$, representing the STM image for negative bias. One can see that bright contrast, which corresponds to the high electron concentration, is observed on some of In atom sites. It should be noted that the bright contrast is not obtained near all of the In sites on the surface. Also the bright contrast is not observed at the Ag and Ca sites. This is because Ag and Ca atoms on the surface layer intrude slightly into the bulk in comparison with In. For the model B1, we have additional bright contrast on In atoms in the tetrahedral cluster on the surface. We expect that the STM study with atomic resolution may clarify atomic arrangements at the cluster center more precisely.

Figure 3 shows the charge distribution calculated from the unoccupied states within 1 eV
Figure 2. Charge distribution calculated from the occupied states within 1 eV below $E_F$, representing the STM image for negative bias. Bright contrast is observed on a different subset of the In sites from those giving the bright contrast for negative bias. In addition to point-like contrast corresponding to a single In atom, we have textured weak contrast. This contrast is made from the charge distribution around Ca and Ag sites in the surface layer. If one chooses the bias voltage larger, more strong contrast is obtained near the Ca sites because of large contribution from the low-lying unoccupied Ca-3d states.

Figure 3. Charge distribution calculated from the unoccupied states within 1 eV above $E_F$, representing the STM image for positive bias. The charge distribution of the slab model on a vertical section is shown in Fig. 4. The charge density is calculated from the occupied states within 1 eV below $E_F$ on a plane at $x = 0.5$ for the model B1. Electron cloud extends towards the vacuum around the topmost In on the surface and this gives bright contrast in Fig. 2. The electron distribution is also enhanced between atoms inside the slab and such rearrangement of the charge density may contribute to stabilization of the surface. For cubic approximants Cd$_6$M (M=Yb, Ca), it is known that the low-lying unoccupied d-states of the second element M are indispensable for compound formation and the sp-d hybridization between the Cd-5p states and the low-lying d-states of M plays an essential role in cohesion [4]. We compare the charge distribution with that for a hypothetical slab model where Ca is replaced with Mg, which has no low-lying unoccupied atomic d-states (Fig. 4). One can see that the characteristic charge distribution between atoms near the surface is significantly reduced in the hypothetical slab with Mg. This suggests that the low-lying unoccupied Ca-3d states contribute to the occupied states stabilizing the surface.
Figure 4. Charge distribution calculated from the occupied states on a plane at $x = 0.5$ for (a) Ag-In-Ca and (b) hypothetical Ag-In-Mg. Atoms on the plane are shown in red, green and blue, respectively, for Ag, In and Ca in (a) and substituted Mg is shown in purple in (b).

4. Conclusion

Surface properties and stability of QC-related complex metallic compounds has been studied theoretically. Electronic structures are calculated by the first-principles method for a slab of Ag-In-Ca cubic approximant. A slab model is constructed by terminating the bulk structure of a cubic approximant at a flat (001) plane intersecting the cluster center. Optimal structures of surface is obtained by relaxing the atoms to their force-free positions. It is found that, after relaxation, In is at topmost position near the vacuum, Ag intrudes into the bulk and Ca is located at intermediate layers between In and Ag. To simulate STM images for the slab model, we calculate the charge distribution from the electronic states in an appropriate energy range. We find that bright contrast is observed on different subsets of the In sites for the charge distributions calculated from occupied and unoccupied states. This suggests that STM images change depending on sample bias voltage but they must be carefully interpreted because the difference is not necessarily due to differences in atomic species or height of the atomic positions. By comparing the charge distribution with a hypothetical Ag-In-Mg slab model, we conclude that the low-lying unoccupied Ca-3d states contribute to stabilizing the surface.

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