Atomic and electronic structures of the Au₂Sn surface alloy on Au(111)Jalil Shah¹, W. Wang^{2*}, Hafiz M. Sohail, and R. I. G. Uhrberg^{1†}¹Department of Physics, Chemistry and Biology, Linköping University, S-581 83 Linköping, Sweden

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Atomic and electronic structure investigations of the substitutional Au₂Sn surface alloy formed on Au(111) are presented. Low energy electron diffraction and scanning tunneling microscopy (STM) reveal a structure with a local $\sqrt{3} \times \sqrt{3}$ periodicity with a superimposed modulation resulting in a $26 \times \sqrt{3}$ unit cell. STM images show a striped structure that resembles the herringbone reconstruction of clean Au(111), but with a longer periodicity compared to the $22 \times \sqrt{3}$ unit cell of clean Au(111). Angle-resolved photoelectron spectroscopy data along the high-symmetry lines $\bar{\Gamma} - \bar{K}' - \bar{M}'$ and $\bar{\Gamma} - \bar{M}' - \bar{\Gamma}'$ of a $\sqrt{3} \times \sqrt{3}$ surface Brillouin zone show two bands from the Au₂Sn surface alloy layer. The experimental bands are compared to the calculated band structure of the local $\sqrt{3} \times \sqrt{3}$ periodicity. Most of the experimental band dispersions are qualitatively reproduced by the theoretical band structure including a spin split of one of the alloy bands. However, our detailed data reveal a band split, not present in the calculated bands of the $\sqrt{3} \times \sqrt{3}$ model, which is a consequence of the striped atomic structure of the Au₂Sn surface alloy.

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I. INTRODUCTION

Binary surface alloys constitute a type of two-dimensional (2D) material that has been subjected to significant interest recently. This is particularly so in the case of surface alloys formed by substitution of one out of three atoms of (111) surfaces of noble metals forming a $\sqrt{3} \times \sqrt{3}$ periodicity. Several studies have focused on spin-orbit splitting (Rashba split [1]) of the band structure resulting from the formation of surface alloys by the heavier elements in Groups IV (Pb) and V (Sb, Bi). These elements and Sn form surface alloys that are confined to the topmost atomic layer with a plain $\sqrt{3} \times \sqrt{3}$ reconstruction, where each unit cell contains one alloy atom and two substrate atoms in an ordered fashion. In most studies, the surface alloys have been prepared on Ag(111) including Ag₂Ge [2–4], Ag₂Sn [5], Ag₂Pb [6], Ag₂As [7], Ag₂Sb [8], and Ag₂Bi [9]. A large Rashba type of spin split was reported for Ag₂Bi [9], while a smaller split was observed for Ag₂Pb [6], and a barely observable one was reported for Ag₂Sb [8]. In contrast to Sn, Pb, Sb, and Bi, the Ge and As atoms result in a surface alloys with complex striped structures superimposed on the $\sqrt{3} \times \sqrt{3}$ periodicity. As a consequence of the higher order periodicity, there is a split of one of the alloy bands at the $\bar{M}$ point of a $\sqrt{3} \times \sqrt{3}$ surface Brillouin zone (SBZ) [2–4,7]. Au(111) is an alternative substrate for the formation of sub-

stitutional surface alloys. The clean Au(111) surface differs, however, from the Ag(111) surface by showing a complex reconstruction that can be described by a large rectangular unit cell, i.e., the so-called herringbone reconstruction described by a $22 \times \sqrt{3}$ rectangular unit cell [10–14]. The formation of Au-Sn alloys on Au(111) has been reported in some recent papers [15–18]. The experimental and theoretical study by Maniraj *et al.* [15], reports atomic and electronic properties of the Au₂Sn $\sqrt{3} \times \sqrt{3}$ surface alloy with 1/3 monolayer (ML) of Sn. Other studies report atomic and electronic structure data from Au-Sn alloys with different amounts of Sn, showing other periodicities denoted AuSn p(3 × 3)R15° [17,18], Au₂Sn $\sqrt{3} \times \sqrt{7}$ [16,17], and Au_{5,1}Sn $\sqrt{3} \times \sqrt{3}$ [18].

In this paper, we present a study of the atomic and electronic structures of the Au₂Sn surface alloy formed by substitution of 1/3 ML of Au by Sn atoms in the uppermost layer of Au(111). Low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) data revealed an atomic structure showing a striped $\sqrt{3} \times \sqrt{3}$ structure with a periodicity corresponding to a $26 \times \sqrt{3}$ unit cell. Two electronic bands of the surface alloy were identified in the data from angle-resolved photoelectron spectroscopy (ARPES). The dispersions of these bands were found to be in good agreement with a theoretical band structure of a plain $\sqrt{3} \times \sqrt{3}$ model [15]. In particular, a theoretically predicted spin-split was supported by our experimental data. The ARPES data showed, however, more details than predicted by the plain $\sqrt{3} \times \sqrt{3}$ calculations. A band split induced by the striped structure was also found.

II. EXPERIMENTAL AND THEORETICAL DETAILS

The experiments were performed at room temperature in three separate experimental setups. All three setups were equipped with LEED. STM images were recorded at Linköping University using a variable temperature STM from

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Omicron. ARPES data were obtained at beamline I4 at MAX-lab, using a Phoibos 100 2D-analyzer from Specs, and at the Bloch beamline of MAX IV, using a Scienta DA30L analyzer. The angular and energy resolutions were 0.3° and ~ 50 meV, respectively.

An Au(111) single crystal was cleaned by repeated cycles of Ar^+ ion sputtering (1 keV) followed by annealing at 400°C until sharp 1×1 LEED spots were obtained. The 1×1 spots were surrounded by well-defined satellite spots characteristic of the $22 \times \sqrt{3}$ reconstruction of clean Au(111). To prepare the Au_2Sn surface alloy, the Au(111) sample was kept at a temperature of 230°C while $1/3$ ML of Sn was deposited. After cooling down to room temperature, LEED showed a new set of satellite spots around 1×1 spots and several spots around $\sqrt{3} \times \sqrt{3}$ positions.

First-principles density functional theory (DFT) calculations were used to interpret the experimental electronic structure data from ARPES. Atomic structures were modeled by a slab, which was built from 23 Au layers terminated by a $\text{Au}_2\text{Sn}\sqrt{3} \times \sqrt{3}$ supercell on each surface with inversion symmetry. About $25 \text{ \AA}$ of vacuum spacing was used to avoid interaction between neighboring slabs of the periodic structure. The positions of all atoms were fully relaxed using the functional of Perdew, Burke and Ernzerhof [19] and the projector augmented wave method within Vienna *ab initio* simulation package (VASP) code [20]. The energy cutoff of the plane-wave basis set was 365 eV, and the k -point mesh was $(2 \times 2 \times 1)$. All atoms were relaxed until the average force was within $0.03 \text{ eV/\AA}$. Band structure calculations were implemented considering spin-orbital coupling. After full relaxation, the location of the Sn atom is $\sim 0.09 \text{ \AA}$ lower than the two Au atoms on the surface.

III. RESULTS AND DISCUSSION

A. Low energy electron diffraction

Figure 1(a) shows a LEED pattern of clean Au(111) which acts as a substrate for the formation of the Au_2Sn surface alloy. The pattern consists of sharp 1×1 spots surrounded by several satellite spots originating from the so-called herringbone reconstruction of the clean surface. The periodicity of this reconstruction is usually described by a rectangular $22 \times \sqrt{3}$ unit cell corresponding to a uniaxial compression of the surface layer along $\langle 101 \rangle$ directions. The prevailing atomic model has 23 Au atoms squeezed into a distance corresponding to 22 second-layer atoms located at bulk positions. The $22 \times$ superperiodicity results in diffraction spots along three lines separated by 120° . As a result, these satellite spots form hexagons that surround each 1×1 spot, as is clear from the inset of Fig. 1(a). One can note that the orientation of the satellite hexagons is 90° different from the hexagon formed by the 1×1 spots.

LEED patterns of the Au_2Sn surface alloy are shown in Figs. 1(b) and 1(c) after annealing to nearly 300°C to improve the quality after the initial preparation. Compared to the clean Au(111) surface, LEED from Au_2Sn shows a clear difference near 1×1 spots as is evident from the insets of Figs. 1(a) and 1(b). In addition, there are several diffraction spots located around $\sqrt{3} \times \sqrt{3}$ positions. The arrangement of these

FIG. 1. (a) LEED pattern (127 eV) from the clean Au(111) sample. The inset shows details of the diffraction due to the so-called herringbone reconstruction described by a rectangular $22 \times \sqrt{3}$ unit cell (60 eV). (b) LEED pattern (52 eV) from the Au_2Sn surface alloy. The red arrow points at diffraction near a 1×1 position of Au(111), also shown enlarged by the inset. The green arrow points at diffraction around a $\sqrt{3} \times \sqrt{3}$ position. The diffraction spots closest to $\sqrt{3} \times \sqrt{3}$ positions form a small triangle. The insets of (a) and (b) illustrate the difference in the satellite pattern surrounding the 1×1 spots of clean Au(111) and of the Au_2Sn surface alloy. (c) LEED pattern (28 eV), showing details of the diffraction around $\sqrt{3} \times \sqrt{3}$ positions. (d) The left part of the figure shows a zoom-in of the LEED pattern inside the red rectangle in (c). The right part shows schematic, three domain, diffraction patterns from $25 \times \sqrt{3}$, $26 \times \sqrt{3}$ and $27 \times \sqrt{3}$ periodicities. Characteristic arrangements of spots are indicated by the shapes drawn by red lines. The schematic LEED pattern for the $26 \times \sqrt{3}$ periodicity agrees with the experimental LEED pattern.

diffraction spots is clearer at lower electron energies as illustrated by Fig. 1(c). This LEED pattern resembles qualitatively the pattern observed for the striped Ag_2As surface alloy [7], which suggests that also the Au_2Sn surface alloy has a striped structure. Figure 1(d) shows a zoom-in of the diffraction around the $\sqrt{3} \times \sqrt{3}$ position indicated by the red frame in Fig. 1(c). A schematic LEED pattern for three domains of a $26 \times \sqrt{3}$ periodicity is shown to the right of the experimental LEED pattern in Fig. 1(d). The LEED pattern and the schematic diffraction pattern have been drawn to scale, which was achieved by overlapping 1×1 “spots”. The inner triangle and the distorted hexagon, indicated by red lines in the schematic diffraction pattern of the $26 \times \sqrt{3}$ periodicity, fit very well with the positions of the diffraction spots in the LEED pattern. Nearby periodicities result in qualitatively different patterns. $27 \times \sqrt{3}$ generates one spot at the $\sqrt{3} \times \sqrt{3}$ position surrounded by six spots forming a hexagon, while $25 \times \sqrt{3}$ results in a spot pattern rotated by 60° compared to the experimental LEED pattern. $23 \times \sqrt{3}$ and $29 \times \sqrt{3}$ unit cells would generate spot patterns around $\sqrt{3} \times \sqrt{3}$ positions in qualitative agreement with the experimental LEED pattern,

FIG. 2. Atomically resolved empty state STM image obtained at room temperature from a $22.4 \times 22.4 \text{ nm}^2$ area (tunneling current: 200 pA and sample bias: 250 mV). A local $\sqrt{3} \times \sqrt{3}$ unit cell is shown by the white diamond while the white rectangle labeled $26 \times \sqrt{3}$ is the best fit to the periodicity of the striped structure. See the text for the discussion of the $23 \times \sqrt{3}$ and $29 \times \sqrt{3}$ unit cells. The yellow rectangle shows the size of the $22 \times \sqrt{3}$ cell of the clean Au(111) surface for comparison.

but the sizes of these unit cells do not agree with STM data, see below.

B. Scanning tunneling microscopy

STM was used to obtain information about the atomic structure of the Au_2Sn surface alloy. A striped structure that resembles that of the herringbone structure on clean Au(111) was revealed by STM. An atomically resolved STM image is displayed in Fig. 2. The striped structure formed by the brighter parts of the image is quite clear. In similarity with the clean Au(111) surface, the stripes are separated by alternating short and long distances resulting in a pairing of the stripes. Distances between the atomic features correspond to a $\sqrt{3} \times \sqrt{3}$ periodicity and a unit cell is shown by the white diamond. There is one atomic feature per unit cell, which we assign to Sn in accordance with all other reports on this type of surface alloy, i.e., Ag_2Ge , Ag_2Sn , Ag_2Pb , Ag_2As , Ag_2Sb , Ag_2Bi , and Au_2Sn [2–9,15]. The stripes are not perfectly regular which makes it hard to precisely define a unit cell for this superstructure. However, we find the best agreement with the rectangular unit cell shown by white lines, labeled $26 \times \sqrt{3}$, in Fig. 2. The short side corresponds to a $\sqrt{3} \times$ distance and the long side is nine times a $3 \times$ distance. Based on the alloy layer, one would label the unit cell as $27 \times \sqrt{3}$. However, in analogy with clean Au(111), one can assume that the striped structure corresponds to a uniaxial compression of the alloy layer. In the case of clean Au(111), 23 surface atoms are squeezed into a distance corresponding to 22 second layer atoms. Applying this model to Au_2Sn , we suggest that 27 atoms of the alloy layer occupy a distance equivalent to that of 26 second layer atoms. Thus, the unit cell of the striped phase should be denoted $26 \times \sqrt{3}$ with respect to an ideal Au(111)

1×1 surface. This is consistent with the LEED data, from which a $26 \times$ superperiodicity was concluded. The $23 \times \sqrt{3}$ and $29 \times \sqrt{3}$ unit cells, mentioned in Sec. III A, do not fit with the striped structure of the STM image as illustrated in Fig. 2. A $22 \times \sqrt{3}$ unit cell is also included in Fig. 2 (yellow lines) to illustrate the difference in the periodicity of the clean Au(111) surface and that of the Au_2Sn surface alloy. Our LEED and STM results differ from those presented in Ref. [15]. In contrast to that study, we find that the Au_2Sn surface alloy has a striped structure with a periodicity that is larger than that of the herringbone structure of the clean Au(111) surface. The alloying with 1/3 monolayer of the slightly larger Sn atom (covalent atom radius of 1.45 Å compared to 1.35 Å for Au) has resulted in a change from a $22 \times$ to a $26 \times$ periodicity.

C. Angle-resolved photoelectron spectroscopy

ARPES was used to study the electronic structure of the clean Au(111) sample as a reference for the interpretation of the ARPES data from the Au_2Sn surface alloy. Figures 3(a) and 3(b) show data obtained along the two high-symmetry directions $\bar{\Gamma} - \bar{M}$ and $\bar{\Gamma} - \bar{K}$ of the 1×1 SBZ of Au(111), respectively. The 1×1 and the $\sqrt{3} \times \sqrt{3}$ SBZs, used when discussing the Au_2Sn data below, are illustrated in Fig. 3(c). The ARPES data show emission from the Shockley surface state, S, centered at $\bar{\Gamma}$. This surface state exhibits a spin-orbit splitting which is clearly observed in Fig. 3(d), in agreement with reports in the literature [10,12–14]. Beside the Shockley state, all other features in Figs. 3(a) and 3(b) correspond to emission from 3Dbulk bands. The emission in the region below $\approx -2 \text{ eV}$ originates from the $5d$ bands, while the dispersive features, labeled B, are due to emission from the bulk s,p bands.

ARPES data from the Au_2Sn surface alloy is shown in Fig. 4 in the form of constant energy contours at 0.1 eV below the Fermi level (E_F). There are two contours, S1 and S2. The inner one has a distorted hexagonal shape, while the outer contour has a flowerlike shape. These shapes are similar to what has been reported for Ag_2Sn [6], compare Figs. S1(a) and S1(b) in the Supplemental Material [21]. Ag_2Sn , which forms a plain $\sqrt{3} \times \sqrt{3}$ structure, exhibits, however, sharp contours for the two alloy states, while the contours of Au_2Sn appear fuzzy. A closer look reveals the existence of two sub contours for each one of S1 and S2, pointed out by the arrows in Fig. 4. This additional complexity of the contours resembles what has been reported for Ag_2Ge [2], see Fig. S1(c) in the Supplemental Material [21]. The complex shapes of the constant energy contours for Ag_2Ge are related to a striped structure superimposed on the $\sqrt{3} \times \sqrt{3}$ periodicity. The two S1 sub contours for Au_2Sn coincide along $\bar{\Gamma} - \bar{K}'$, while they are clearly separated along $\bar{\Gamma} - \bar{M}'$. As a consequence, the S1 band of Au_2Sn is expected to appear as split close to the E_F in the $\bar{\Gamma} - \bar{M}'$ direction, but not along $\bar{\Gamma} - \bar{K}'$.

Energy versus $k_{\parallel}$ dispersions ($E(k_{\parallel})$) obtained by ARPES from Au_2Sn are shown in Figs. 5(a) and 5(b) for the two high-symmetry lines $\bar{\Gamma} - \bar{K}' - \bar{M}'$ and $\bar{\Gamma} - \bar{M}' - \bar{\Gamma}'$ of the $\sqrt{3} \times \sqrt{3}$ SBZs illustrated in Fig. 3(c). First of all, one can note that the Shockley state of the clean Au(111) surface is absent in the emission from the Au_2Sn alloy, while the strong emission from the bulk s,p bands, B, is still observed.

FIG. 3. (a) and (b) ARPES data obtained with a photon energy of 26 eV along the two high-symmetry directions $\bar{\Gamma} - \bar{M}$ and $\bar{\Gamma} - \bar{K}$ of the 1×1 surface Brillouin zone (SBZ) of Au(111), respectively. The dispersive structure, S, shows the Shockley surface state that is located in the gap of the projected bulk band structure around $\bar{\Gamma}$. The highly dispersive features, labeled B, correspond to emission from bulk s,p bands. Below ≈ -2 eV there is contribution from the 5d bands. (c) 1×1 and $\sqrt{3} \times \sqrt{3}$ SBZs with symmetry point labels. (d) Detailed data showing a well-resolved spin-orbit split of the Shockley surface band.

Along $\bar{\Gamma} - \bar{K}' - \bar{M}'$, there are two dispersive bands that we identify as S1 and S2 appearing in the constant energy data in Fig. 4. The S1 band crosses the Fermi level at $\approx \pm 0.2 \text{\AA}^{-1}$ and disperses steeply downward away from $\bar{\Gamma}$. S2 appears as a weak band with a steep downward dispersion outside of S1. Both S1 and S2 are more clear in the $k_{||}$ range 2.0 to $2.4 \text{\AA}^{-1}$. The separation between S1 and S2 is small in agreement with the constant energy contour data in Fig. 4. The band with a local maximum at $\bar{M}'$ is identified as S2 as

FIG. 4. Constant energy contours recorded from Au_2Sn at 0.1 eV below E_F using a photon energy of 26 eV. Two contours, labeled S1 and S2, are observed. The inner, distorted hexagon, and the outer, flowerlike contour, resemble the contours observed for Ag_2Sn [5]. However, the S1 and S2 contours of Au_2Sn are not single contours as in the case of Ag_2Sn . The red arrows indicate separations of each contour into two sub contours.

in the case of Ag_2Sn . The S1 and S2 bands are also identified along $\bar{\Gamma} - \bar{M}' - \bar{\Gamma}'$, see Fig. 5(b). The emission intensities of these bands are strong in the second SBZ in the $k_{||}$ range 1.6 to $2.2 \text{\AA}^{-1}$. This behavior of the intensity was also observed for Ag_2Sn [5]. The separation between the S1 and S2 bands is larger in this direction in accordance with the constant energy contours in Fig. 4. As indicated by the two green arrows, S1 appears as two bands along $\bar{\Gamma} - \bar{M}'$, which is expected from the split of the constant energy contour. The S2 band disperses to a minimum of ≈ -1.2 eV at the $\bar{M}'$ point ($k_{||} = 2.18 \text{\AA}^{-1}$), which corresponds to the maximum energy of S2 at $\bar{M}'$ along $\bar{\Gamma} - \bar{K}' - \bar{M}'$. The dispersion of S2 has consequently a saddle point at $\bar{M}'$. An interesting feature is present in the lower part of the S1 dispersion at negative $k_{||}$ values where the band shows a clear split into two branches between -0.9 and $-1.2 \text{\AA}^{-1}$, indicated by the two red arrows. Apart from the bands originating from the Au_2Sn surface alloy there are two dispersive features labeled BU, which appear at places consistent with umklapp scattered bulk emission. The Ag_2Pb $\sqrt{3} \times \sqrt{3}$ surface alloy is the clearest example of umklapp scattering of bulk emission, see Ref. [6] and Fig. S1(d) in the Supplemental Material [21].

Along $\bar{\Gamma} - \bar{K}' - \bar{M}'$ in the negative $k_{||}$ direction, one can note that S2 is split into two branches, S2- and S2+. This type of split has been observed for the corresponding band on striped phases of Ag_2Ge [2–4] and Ag_2As [7], but is not observed for the plain $\sqrt{3} \times \sqrt{3}$ structure of the Ag_2Sn surface alloy.

To gain further insight into the electronic structure of the Au_2Sn surface alloy, band structure calculations were performed based on DFT including spin-orbit coupling. The large $26 \times \sqrt{3}$ cell, concluded from LEED and STM data, is simply too large for meaningful calculations. A $\sqrt{3} \times \sqrt{3}$ model, which corresponds to the local structure, was used instead. Having said that, one should be aware that

FIG. 5. (a) and (b) ARPES data from Au_2Sn along the $\bar{\Gamma} - \bar{K}' - \bar{M}'$ and $\bar{\Gamma} - \bar{M}' - \bar{\Gamma}'$ lines of the $\sqrt{3} \times \sqrt{3}$ SBZs, respectively. The data were obtained at room temperature using a photon energy of 27 eV. Dispersive features labeled B originate from three-dimensional bulk bands of Au(111). The labels S1 and S2 are used to denote the two bands originating from the 2D Au_2Sn surface alloy. A few observations of particular interest are indicated by arrows pointing at each other, i.e., the split of S1 in (b) (red arrows), and the fuzzy appearance of the S1 band in the first SBZ in (b) (green arrows). (c) and (d) Calculated band structure for the $\sqrt{3} \times \sqrt{3}$ model of the Au_2Sn surface alloy in (e). Red, green, and blue symbols show contributions from s, p, and d states, respectively. (e) Relaxed $\sqrt{3} \times \sqrt{3}$ model. Au and Sn atoms in the surface alloy layer are indicated by yellow and grey, respectively. Au atoms in the second and third layers are shown by red and blue, respectively.

the $\sqrt{3} \times \sqrt{3}$ unit cell is most likely distorted since the alloy layer is compressively strained with 27 atoms in the alloy layer squeezed into a distance of 26 second layer atoms.

Figures 5(c) and 5(d) show the calculated band structure along the $\bar{\Gamma} - \bar{K}' - \bar{M}'$ and $\bar{\Gamma} - \bar{M}'$ symmetry lines, respectively. The three uppermost atomic layers of the relaxed $\sqrt{3} \times \sqrt{3}$ model, used in the calculations, are illustrated in Fig. 5(e). There are two bands, $\Sigma 1$ and $\Sigma 2$, originating from the surface alloy layer. Red, green, and blue symbols show contributions from s, p, and d states, respectively. The calculated bands show a good overall agreement with the experimental bands S1 and S2. The major features are the steep dispersion of $\Sigma 1/\Sigma 1$, the dispersion of $\Sigma 2/\Sigma 2$ with a saddle point at $\bar{M}'$, the smaller separation between $\Sigma 1/\Sigma 1$ and $\Sigma 2/\Sigma 2$ in the $\bar{\Gamma} - \bar{K}'$ direction, and the larger separation along $\bar{\Gamma} - \bar{M}'$. One can note that the calculated $\Sigma 1$ band has a flat region with an energy of 0.02 eV at $\bar{\Gamma}$. The corresponding part of the experimental S1 band is also above the Fermi level and is therefore not observed in the ARPES data. The split of the S1 band along $\bar{\Gamma}' - \bar{M}'$, on the negative $k_{||}$ side of Fig. 5(b), finds an explanation as the spin-orbit split of $\Sigma 1$, indicated by red arrows in Fig. 5(d). Band structure calculations using a

$\sqrt{3} \times \sqrt{3}$ model were presented in Ref. [15] together with ARPES data from Au_2Sn . There is a close qualitative resemblance regarding the shapes of the bands in Ref. [15] and those in Figs. 5(c) and 5(d). However, the identification and discussion of the surface alloy bands differ along the $\bar{\Gamma} - \bar{M}'$ line. The $\Sigma 2$ band along $\bar{\Gamma} - \bar{M}'$, labeled S4 in Ref. [15], was not discussed in relation to the experimental data and their S2 band originates from Au d_{xy} bulk states according to our calculation and should not be associated with the alloy layer. See Fig. S2 in the Supplemental Material [21] for details.

The surface alloy bands calculated from the $\sqrt{3} \times \sqrt{3}$ model, $\Sigma 1$ and $\Sigma 2$ in Figs. 5(c) and 5(d), agree with the dispersions of S1 and S2 in Figs. 5(a) and 5(b) and the split of the S1 band is reproduced by the theoretical band structure. However, the model calculation fails to reproduce the split observed in the ARPES data of the S2 band around $\bar{M}'$. This split is most clear on the negative side of Fig. 5(a) where the emission intensity is low. The same type of splitting has been observed for Ag_2Ge and Ag_2As , which are also striped $\sqrt{3} \times \sqrt{3}$ surface alloys, but it was not observed for plain $\sqrt{3} \times \sqrt{3}$ Ag_2Sn . In the case of Ag_2Ge , it has been suggested that the split is caused by umklapp scattering based

on the assumption that the $\sqrt{3} \times \sqrt{3}$ unit cell of Ag_2Ge is uniformly compressed compared to a $\sqrt{3} \times \sqrt{3}$ unit cell of $\text{Ag}(111)$ [4]. The assumed structure is in contrast to the results in Ref. [2], where it is clearly shown that Ag_2Ge has a striped structure with three domains with different orientation. This was concluded from atomically resolved STM images and sharp, well resolved, LEED patterns. Thus, the idea of a uniformly compressed $\sqrt{3} \times \sqrt{3}$ unit cell, on which the umklapp explanation was based, is not supported by experimental results. We conclude that the splitting is due to a structural modification associated with the striped superstructure.

It is of interest to compare our ARPES data with those presented in Ref. [15], which is the only earlier study of the band structure of the Au_2Sn surface alloy. Experimental dispersions were presented along the $\bar{\Gamma} - \bar{K}' - \bar{M}'$ and $\bar{\Gamma} - \bar{M}' - \bar{\Gamma}'$ symmetry lines. Two bands were observed around $\bar{\Gamma}$ and studied within a $k_{\parallel}$ range of about $\approx \pm 0.8 \text{ \AA}^{-1}$. The band closest to $\bar{\Gamma}$ with Fermi level crossings at $\approx \pm 0.2 \text{ \AA}^{-1}$, in their study is most likely identical to S1 in our study. A second band crossed the Fermi level at $\approx \pm 0.4 \text{ \AA}^{-1}$ and is probably the same as our S2 band. After some analysis, the two rather broad experimental bands were presented as two split bands and discussed in terms of a Rashba-type of splitting along $\bar{\Gamma} - \bar{M}'$ in Ref. [15]. In our study, we report two subcontours in the constant energy data that are associated with S1 near E_F . The separation between the two contours is $\approx 0.04 \text{ \AA}^{-1}$ along $\bar{\Gamma} - \bar{M}'$, which is similar to the separation reported in Ref. [15]. In our case, we interpret the separation into two branches as an effect of the striped $26 \times \sqrt{3}$ structure instead of a Rashba split since the constant energy contours of Au_2Sn resembles those of striped Ag_2Ge and they are different from the Rashba split contours of Ag_2Pb [2], see Fig. S1(d) in the Supplemental Material [21].

IV. SUMMARY

The atomic and electronic structures of the Au_2Sn surface alloy were studied involving LEED, STM, ARPES, and DFT calculations. From LEED and STM, it was concluded that Au_2Sn shows a striped phase with a herringbone type of reconstruction described by a $26 \times \sqrt{3}$ unit cell. The distances between stripes are larger than for the $22 \times \sqrt{3}$ reconstruction of clean $\text{Au}(111)$. STM showed a $\sqrt{3} \times \sqrt{3}$ -like periodicity locally, formed by Sn atoms substituting $1/3$ ML of the Au atoms in the surface layer. As the $26 \times \sqrt{3}$ structure corresponds to a compressed layer it is likely to impose a slight distortion of the $\sqrt{3} \times \sqrt{3}$ unit cell. Constant energy contours obtained by ARPES showed two 2D electronic bands, S1 and S2, originating from the Au_2Sn surface alloy. Their dispersions were mapped along symmetry lines of $\sqrt{3} \times \sqrt{3}$ SBZs. Theoretical band structure calculations, based on a plain $\sqrt{3} \times \sqrt{3}$ model, reproduced the basic features of the dispersions of S1 and S2 and, in particular, a theoretically predicted spin-orbit split of S1 was observed in our ARPES data. In similarity to other striped phases, deviations from the calculated band structure of the plain $\sqrt{3} \times \sqrt{3}$ model were noted. The S1 and S2 contours were doubled. Further, the S2 band was split at $\bar{M}'$ along $\bar{\Gamma} - \bar{K}' - \bar{M}'$ something that is also the case for the striped Ag_2Ge and Ag_2As surface alloys.

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