# **Electronic Supplementary Information**

# Self- texturizing electronic-properties of a 2-dimensional GdAu<sub>2</sub> layer on Au(111): the role of out-of-plane atomic displacement

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#### 1. Sample preparation

The GdAu<sub>2</sub> surface alloy is achieved depositing in ultra-high vacuum conditions (UHV) via electron bombardment gadolinium atoms onto the Au(111) surface previously prepared by cycles of Ar+ ion sputtering and subsequent annealing. The Au(111) surface held at a temperature between 280° and 360°C ensures the formation of ordered GdAu<sub>2</sub> alloy layers. For the realization of this work, the surface was prepared on three different UHV systems. The photoemission and inverse photoemission experiments were performed at room temperature, while the scanning tunneling spectroscopy was performed on the sample hold at 1K in a bath cryostat.

# 2. Intermetallic structure

The GdAu<sub>2</sub> alloy structure was identified as by Corso et al. <sup>1</sup>. According to this work the unit cell of the alloy layer is described in the inset of figure ESI2.1, where the blue circles and the yellow ones represent the Gd and Au atoms of the unit cell respectively.



**Figure ESI2.1. Structure of GdAu**<sub>2</sub>/Au(111). Topographic image of a partial coverage of GdAu<sub>2</sub> on Au(111) showing atomic resolution.Image size 20nm x 11nm. The dashed and dotted lines indicate high symmetry directions of the moiré and Au(111), respectively. The small and large rhombi indicate the alloy and superstructure unit cells, respectively. In the inset, the proposed structure of the GdAu<sub>2</sub> alloy.

Scanning tunneling microscopy images showing simultaneous atomic resolution in the Au(111) surface and in the alloy layer allow determining the angle of rotation of the moiré superstructure and of the alloy layer with respect to the Au(111) surface, as 33° and 5° respectively. Similarly, the periodicity of the alloy and of the moiré superstructure unit cell, depicted with rhombi in figure ESI2.1, have been determined to be 5.3Å and of 37Å respectively. Minor local variations of the supercell size can be detected. These do not affect the density of states as described for the similar structure GdAg<sub>2</sub>/Ag(111) <sup>2</sup> suggesting a different interaction with the substrate.

It is also worth noticing that the border of alloy islands are always terminated by Gd in hollow stacking position with respect to the underlying Au(111) (see main text). Indeed, the apparent topographic minima, i.e. the darker areas of the moiré pattern, are energetically more expensive as described in the main text.

#### 3. Computational methods and supercells structure

All the DFT simulations were carried out at the GGA<sup>3</sup> level using the plane-wave Quantum-Espresso<sup>4</sup> code. The spin-polarized Kohn-Sham equations were solved within the plane wave/pseudopotential framework using Vanderbilt's ultrasoft pseudopotentials<sup>5</sup>, employing basis-set cutoffs of 117 Ry and 579 Ry for the electron wave function and density, respectively. The Brillouin zone of all GdAu<sub>2</sub>/Au(111) computational supercells was sampled with a regular mesh of 8x8 k points. A Hubbard U <sup>6</sup> term acting on the Gd-4f orbitals was added to the GGA energy functional (GGA+U) in all calculations. The values of the U and J parameters (U=6.7 eV J=0.7 eV) were chosen following previous works, so as to provide a reasonable representation of the f-bands energy position in Gd bulk <sup>7-8</sup>. Structural relaxations of the interfaces were performed at the GGA+U level. Here, only the atoms of the three bottom Au layers were kept fixed, while all other atoms were free to move during optimization. The electronic properties were calculated starting from these optimized geometries and performing an additional set of GGA+U calculations that included the spin-orbit interaction. These last calculations

were used for the analysis of the electronic structure, the total and projected density of states, as well as for the interface energetics.

The GdAu<sub>2</sub>/Au(111) system was modeled with a hexagonal supercell having a  $(\sqrt{3}x\sqrt{3})R30^\circ$  orientation with respect to the (1x1) surface lattice of the Au(111) substrate (Fig. ESI3.1). The in-plane lattice constant of the supercell was 5.11 Å, while the out-of-plane one allowed for a region of vacuum between periodic images larger than 10 Å.

The Au(111) substrate was modeled with 5 atomic layers. We considered three different stacking configurations of the  $GdAu_2$  layer with respect to Au(111) substrate. The three stacking configurations are defined as TOP, HPC and FCC following the position of the Gd atoms with respect to the high-symmetry sites of the underlying Au(111) surface.



Figure ESI3.1 Computational cells: the GdAu<sub>2</sub> layer (a) and the supporting Au(111) surface (b).

#### 4. FCC and HCP interface structures

Here we provide evidence that the optimized geometries of the HCP and FCC interface configurations are almost identical. The corresponding structures are shown in Figure ESI4.1, which displays the side and top views of the outermost three layers. The differences in the interfacial vertical distances between the FCC and HCP configurations are lower than 0.01 Å, i.e. smaller than the error bars in DFT calculations (Table ESI4.2).



**Figure ESI4.1 Optimized structural geometry.** Upper panel: Side view of the FCC (a) and HCP (b) geometries. Lower panel: Top view of the FCC (c) and HCP (d) geometries. Only the first three layers are shown. Yellow, red and black colors denotes the Au atoms in the  $GdAu_2$  alloy, and in the first and second Au(111) layers, respectively.

	ТОР	FCC	НСР
$d_z(Gd-Au_1)$	2.8 Å*	2.7 Å	2.7 Å
$d_z(Au_0-Au_1)$	3.0 Å	2.5 Å	2.5 Å
$d_z(Au_1-Au_2)$	2.4 Å	2.4 Å	2.4 Å

**Table ESI4.2. Vertical distances between Gd and Au atoms in the 3 interface configurations**. Au atoms are labeled according to their layer position, see Figure ESI4.1. \* In the TOP configuration dz represents the bondlength between the Gd atom and the underlying atom of the Au1 layer, which is highly distorted and non-planar.

#### 5. Energy of the Gd-f states

To understand the dependence of the Gd f states on the atomic environment, we have computed the Gd-f projected DOS for the following systems: Gd bulk, free standing GdAu<sub>2</sub>, and GdAu<sub>2</sub>/Au(111) interfaces in TOP, FCC and HCP configurations. These PDOS are shown in Fig. S5.1. The Gd-f PDOS was used to compute the weighted mean energy of the Gd f states in these different systems. The values are reported in Table ESI5.2.



**Figure ESI5.1.** Computed total and atom-Projected density of states (DOS and PDOS). Various systems as bulk Gd, free standing GdAu<sub>2</sub> layer, TOP, FCC and HCP GdAu<sub>2</sub>/Au(111), are compared.

Gd-f states	Gd Bulk	GdAu <sub>2</sub> free-standing	ТОР	FCC	НСР
Occupied	-9.2 eV	-9.4 eV	-9.0 eV	-8.8 eV	-8.9 eV
Unoccupied	3.0 eV	3.0 eV	3.3 eV	3.6 eV	3.5 eV

**Table ESI5.2. Mean Energy of the occupied and unoccupied Gd f-states.** The values of Gd bulk, free standing GdAu<sub>2</sub>, and GdAu<sub>2</sub>/Au(111) interfaces in TOP, FCC and HCP configurations are given.

### 6. U dependence

In within the DFT+U approach, the energy of the Gd-f states, on top of being determined by the chemical and crystalline environments, is also controlled by the value of the effective parameter  $U_{eff}$ =U-J. We have performed additional calculations to check how this parameter affects the electronic structure of the GdAu<sub>2</sub>/Au(111) system and in particular the dependence of the Gd-f energies. This analysis was performed on the TOP configuration only, since the same effect is expected for the other ones. We have considered three values of  $U_{eff}$ :  $U_{eff}$ =5, 6, 7 eV. The resulting DOS and PDOS analysis are plotted in Fig ESI6.1. The position of the weighed mean energies of the occupied and unoccupied 4f states are collected in Table S6.2. This analysis shows that a better agreement with the experimental position of the f states in GdAu<sub>2</sub> is obtained by using values of  $U_{eff}$ ~7 eV, therefore larger than those reported for Gd bulk.



Figure ESI6.1 Dependence of the energy of the Gd f states on the value of  $U_{eff}$ . The GdAu<sub>2</sub>/Au(111)/Au(111) TOP interface is taken as a representative case.

Gd-f states	TOP $U_{eff} = 5 \text{ eV}$	TOP $U_{eff} = 6 \text{ eV}$	TOP $U_{eff} = 7 \text{ eV}$
Unoccupied	2.8 eV	3.3 eV	3.7 eV
Occupied	-8.5 eV	-9.0 eV	-9.6 eV

**Table ESI6.2. Weighed mean energy values of the occupied/unoccupied 4f states**. The mean values of GdAu<sub>2</sub>/Au(111)/Au(111) TOP interface as a function of U is given.

#### 7. Orbital Analysis

A detailed orbital analysis in terms of the  $\Gamma$ -PDOS for the s, p, and d orbitals of the Gd and Au atoms is presented in Figure ESI7.1 for the free-standing flat GdAu<sub>2</sub> layer, in Figure ESI7.3 for the supported GdAu<sub>2</sub>/Au(111) system in TOP and FCC configurations (the PDOS refer to the outermost layer only), and in Figure ESI7.2 for free-standing GdAu<sub>2</sub> layers having the same structural distortions of the supported TOP and FCC configurations. These data shows that 1) the GdAu<sub>2</sub> layer electron states laying in the [-2 eV,2eV] region across the Fermi level have primarily Au-p and Gd-d character (Figures ESI7.1-3); 2) in the free-standing layers, with respect to the flat geometry, the TOP and FCC structural distortions induce shifts and reordering of the electron states (Fig. S7.2) and 3) the coupling with the substrate increases the width of all the bands having Au-d, Au-p, Gd-d and Gd-p character (Figures ESI7.3).



**Figure ESI7.1 Total and Projected density of states at Gamma (** $\Gamma$ **-DOS and**  $\Gamma$ **-PDOS).** The s, p, and d orbitals of the Gd and Au atoms of a free-standing GdAu<sub>2</sub> flat layer are shown.



Figure ESI7.2.  $\Gamma$ -DOS and  $\Gamma$ -PDOS for the s, p, and d orbitals of the Gd and Au atoms of free-standing GdAu<sub>2</sub> layer. The structural distortions of the atoms in the free standing layer are the same as in the supported FCC and TOP configurations.



**Figure ESI7.3.**  $\Gamma$ -DOS and  $\Gamma$ -PDOS of supported GdAu<sub>2</sub>/Au(111) system: the s, p, and d orbitals of the Gd and Au atoms in the FCC and TOP configurations are shown in separated panels.

#### 8. Bader charge analysis

The Bader charge analysis for a set of different systems is presented in Table ESI8.1. This data demonstrates the partial ionic character of the Gd-Au bond in the GdAu<sub>2</sub> alloy and that the charge transfer at the GdAu<sub>2</sub>/Au(111) interface is negligible.

	Au Bulk	Gd bulk	GdAu <sub>2</sub>	GdAu <sub>2</sub> /Au	GdAu <sub>2</sub> /Au	GdAu <sub>2</sub> /Au
			Free	ТОР	FCC	НСР
			standing			
Gd		28 e	26.89 e	26.84 e	26.87 e	26.88 e
Au	11 e		11.55 e	11.39 e	11.43 e	11.43 e

**Table ESI8.1. Bader charges computed for the Gd and Au bulk system**. Free-standing GdAu<sub>2</sub> layer, and for the GdAu<sub>2</sub>/Au(111) TOP, FCC and HCP interfaces.

#### 9. Ultra violet photoemission spectroscopy method

Ultraviolet VB photoemission spectra were acquired in an ultra high vacuum (UHV) experimental apparatus (base pressure  $\sim 4x10^{-10}$  mbar), using the He II emission of a conventional He discharge lamp (hv = 40.8 eV) and a hemispherical electron energy analyzer (PSP). Electron-energy distribution curves were measured at room temperature in normal emission geometry, with an overall instrumental energy resolution of  $\sim 0.25$ eV. All binding energy values are referred to the Fermi energy level of the clean gold crystal.

# 10. Inverse Photoemission electron spectroscopy

The Normal Incidence IPS measurements were performed in the UHV system of IOM SIPE laboratory by using an Erdman-Zipf electron gun, with the electron beam divergence  $< 3^{\circ}$ . Photons emitted from the sample surface are collected by a Geiger-Müller detector with a He-I<sub>2</sub> gas mixture and a SrF<sub>2</sub> entrance window filtering photons at energy hv = 9.5 eV. Current on the sample was  $< 1 \mu A$ . The overall resolution was < 300 meV, as measured by the Fermi level onset of a clean Ta foil.

Spectra are normalized at each point to the incident electron beam current. Measurements have been obtained at normal incidence, at room temperature.

The 4f unoccupied states show strong cross section dependence from the detected photon energy <sup>9</sup>. Nevertheless the filled Gd 4f states present a binding energy close to the detection photon energy of our Geiger Mueller detector (9.5 eV). The increase of the cross section is due to the resonance effect which allows our assignment<sup>10</sup>. The observed Gd 4f empty states at about 4 eV are fully compatible with the values reported in literature <sup>11</sup>.

# 11. Map of density of state

In Figure ESI11.1, topographic and density of states maps achieved simultaneously at selected energies are shown. Aim of this is the identification of the spatial localization of the density of states maxima. This allows distinguishing the major contribution of TOP and HOLLOW sites in the total density of states as highlighted by the corrugation profile (right column).



**Figure ESI11.1: Comparison of topographic and density of states maps at defined energy.** Topographic images (left columns) and corresponding density of sates maps at the indicated energy (a) 3.2eV; (b) 2,75eV; (c) 650meV. Image size: 30nm x 15nm. The blue and green lines highlight the spatial correlation between the topographic positions and the density of state maxima, respectively.

#### 12. Temperature effects on the electron density of states

In Figure ESI12.1, we show the temperature evolution of the low energy density of states at TOP and HOLLOW position in the GdAu<sub>2</sub>/Au(111). It is worth noting that the peak which appears split in TOP position at low temperature becomes a sharp peak as the temperature increases (bottom to top curve). Vice versa, the feature observe in the HOLLOW positions broadens and split as a function of increasing temperature. This suggests that although the feature is observed at the same energy, the orbital character of this feature differs in the two cases highlighting the role of the crystal field in the two atomic stacking configurations.



Figure ESI12.1. Temperature of effect on the density of states. Series of spectra showing the different behavior of the low energy peak of  $GdAu_2/Au(111)$  as a function of increasing temperature (from bottom to top).

# 13. References

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