Spin-Flip and Element-Sensitive Electron Scattering in the BiAg₂ Surface Alloy

Supplementary Material

S. Schirone,¹ E. E. Krasovskii,^{2,3,4} G. Bihlmayer,⁵ R. Piquerel,¹ P. Gambardella,^{1,6,7} and A. Mugarza¹

¹Catalan Institute of Nanoscience and Nanotecnology (ICN2), UAB Campus, E-08193 Bellaterra, Spain

²Departamento de Física de Materiales, Facultad de Ciencias Químicas,

Universidad del Pais Vasco/Euskal Herriko Unibertsitatea,

Apartado 1072, San Sebastián/Donostia, 20080 Basque Country, Spain

³Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4,

San Sebastián/Donostia, 20018 Basque Country, Spain

⁴IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain

⁵Peter Grünberg Institut and Institute for Advanced Simulation,

Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

⁶Instituciò Catalana de Recerca i Estudis Avancats (ICREA), E-08193 Barcelona, Spain

⁷Department of Materials, ETH Zurich, Hönggerbergring 64, CH-8093 Zurich, Switzerland

(Dated: March 23, 2015)

Corresponding author: A. Mugarza (aitor.mugarza@icn.cat)

CONTENTS

I.	Background subtraction	2
II.	Band parameters	2
III.	Scattering at different step types	3
IV.	Fit of the spatial distribution of resonances	3
V.	Lateral shift of resonances	5
VI.	Band structure calculations	6

I. BACKGROUND SUBTRACTION

The interference patterns of BiAg₂ surface states cannot be as easily detected as in other metal surface states [20,21], especially due to the strongly decaying DOS of Rashba-split bands that superpose to the resonant peaks [19]. In order to enhance the resonant features we subtract a reference spectra that represents the DOS of 2D electrons in infinite terraces, acquired more than 300 Å away from any scatterer. This way we also minimize the contribution of the tip DOS [20]. Examples of dI/dV spectra before and after subtraction are represented in Fig. S1a. The top graph shows spectra acquired at the center and side of a small terrace with quantized states (see the whole set of spectra in Fig. S1b), together with the reference spectra (black curve). In the spectra of the small terrace, weak resonances appear on top of the background. Note that the two intense peaks at +731 meV and -100 meV are not related to quantization but to the fast variation of the DOS of Rashba-split bands (they also appear in the reference spectra) [19]. In the subtracted spectra of the bottom graph, the resonances are substantially enhanced and, without the main peaks of the 2D DOS, they can be more easily identified. Note that odd (even) resonances are more pronounced in the center (side) spectra.



FIG. S1. a) Top: Comparison of a reference dI/dV spectra that represents the 2D DOS with spectra taken at a small terrace and show resonances corresponding to the quantization. The reference spectrum (black) is acquired on the center of a large terrace, more than 300 Å away from any scatterer, to avoid any oscillation in the DOS related to interferences. Bottom: Spectra of the top graph after subtraction of the reference spectrum. The resonant peak appear enhanced, at energies close to that of an infinite quantum well of the terrace size (vertical dashed lines). b) Series of subtracted spectra from where the examples of (a) are selected (vertical lines).

II. BAND PARAMETERS

The parameters needed to determine the dispersion of Rashba-split 2D parabolic bands are the band onset E_0 , effective mass m_{eff} , and Rashba energy E_R . The latter, defined as the energy of the band crossing point with respect to the onset, is a measure of the band splitting. We obtain E_0 , E_R and m_{eff} combining two fits: i) the dI/dV spectra with the DOS of Rashba-split 2D parabolic bands [19]; and ii) the FT-STS data with a parabola, after transforming the scattering vectors into wave vector k. We do that by assuming parabolic dispersion, as confirmed by the ab-initio results, which allows the convertion of the scattering vectors into momentum as q = 2k. The first fit is of the integrated DOS and is therefore not very sensitive to m_{eff} . The FT-STS data, on the other hand, is not reliable at small k, and therefore the second fit is not accurate for the determination of E_0 . The most accurate parameters will then be determined by using the dI/dV fit to get E_0 and E_R , and then fixing E_0 in the dispersion fit in order to get an accurate m_{eff} . We limit our analysis to the unoccupied band, since the occupied one deviates considerably from parabolic dispersion due to hybridization at the outer branch. Figure S2 shows the results for both fits. The values we obtained for the parameters are listed in Table SI. Although the values for E_0 and E_R are close to that obtained in a similar fit of the dI/dV in Ref. [16], our value for m_{eff} is smaller by a factor of 2. We note that this seems to be related to the fact that they obtain the value by directly fitting the FT-STS data, without converting the scattering vector to momentum by q = 2k.

$E_0 \text{ (meV)}$	E_R (meV)	m_{eff}
731 ± 0.9	171 ± 2	-0.16 ± 0.01

TABLE SI. Band parameters obtained from the fitting of Fig. S2.



FIG. S2. a) Fit of a dI/dV spectrum obtained in a region away from scatterers using the DOS of Rashba-split parabolic bands [19]. b) Fit of the energy dispersion by using the E_0 obtained in (a). The fit has been performed using the full data range. Discarding the weakest points in the FT-STS data of Fig. 2 ($k > 0.15 \text{ Å}^{-1}$, $q > 0.30 \text{ Å}^{-1}$), we obtain a deviation of 6% in m_{eff} (±0.01).

III. SCATTERING AT DIFFERENT STEP TYPES

The different scattering properties of each step type can be directly appreciated in dI/dV maps acquired in regions where *A* and *B* steps coexist, such as in the example shown in Fig. S3. In the dI/dV map, the intensity of the QPI patterns arising from *A* steps is significantly stronger, indicating larger reflection coefficients for this step type. This is latter confirmed in the Fabry-Pérot analysis of the quantum well resonances (section IV and Fig. 4 of the main text).



FIG. S3. (a) Topography and (b) dI/dV map acquired simultaneously at 0.2V, showing interference patterns formed by A and B steps. Image size: $40.6 \times 40.6 \text{ nm}^2$. Setpoint: I = 0.59 nA, $V_b = 0.2 \text{ V}$.

IV. FIT OF THE SPATIAL DISTRIBUTION OF RESONANCES

The quantized interference patterns that can be observed in the small terrace of Fig. 2(a) arise from multiple scattering within two parallel steps. These can be fit to Fabry-Pérot resonances using the proportional relation $dI/dV(E, x) = C \cdot LDOS(E, x)$. Extending the Fabry-Pérot expression for the local DOS (LDOS) of a confined two-dimensional electron gas proposed by Bürgi et al. [23] to the case of Rashba-split bands, we obtain:

$$LDOS(E, x) = \rho_b + \frac{\rho_s}{\pi} \int_{k_R}^{k_E} dk_x \frac{1}{\sqrt{k_E^2 - (q/2)^2}} \times \left\{ \frac{(1 - r_l^2) \left[1 + r_r^2 + 2r_r \cos\left(qL\left(x - \frac{1}{2}\right) - \varphi_r\right)\right]}{1 + r_l^2 r_r^2 - 2r_r r_l \cos\left(qL + \varphi_r + \varphi_l\right)} + \frac{(1 - r_r^2) \left[1 + r_l^2 + 2r_l \cos\left(qL\left(x + \frac{1}{2}\right) + \varphi_l\right)\right]}{1 + r_l^2 r_r^2 - 2r_r r_l \cos\left(qL + \varphi_r + \varphi_l\right)} \right\},$$
(1)

where $k_E = k - k_R = \sqrt{2m_{\text{eff}}/\hbar^2(E - E_0)}$ and $q = 2(k_x - k_R)$. E_0 , k_R and m_{eff} are the band onset, Rashba momentum shift and effective mass respectively, x is the distance from the center of the terrace in the direction perpendicular to steps, ρ_b and ρ_s are the bulk and surface contributions to the surface DOS, L is the width of the resonator, and $r_{l/r}$ and $\phi_{l/r}$ are the reflection coefficient and phase shift at the left/right barriers. Absorption enters in the equation by the probability conservation $|r|^2 + |t|^2 + |a|^2 = 1$ (note that this allows non-transmitting resonant states, i.e. $\phi = \pm \pi$, with r < 1). In this model, reflection affects the intensity of the interference patterns, whereas transmission directly relates to the phase shift and hence determines the spatial modulation along x.

A finite transmission results in an overall stretch of the resonant wavefunction beyond the potential barriers. The main effects are: i) non-zero value of the wave function beyond the resonator walls; ii) outwards lateral shift of off-centered maxima. Our fit is insensitive to the former due to the strong edge-related signal beyond $|(x - x_c)/L| > 0.35$ that overlaps with the resonance. Thus, the most reliable features for the fit are the off-centered peak maxima. These are missing in the N=1 resonance, and hindered by the edge-related signal for N = 3. On the contrary, the peak maxima of the N = 2 resonance is clearly visible, which makes its fitting the most reliable. For this reason we limit our fit analysis to N = 2.

The reflection coefficients cannot be univocally determined from our analysis due to the fact that, in the limited fitting region away from the resonator walls, the effects of $r_{l,r}$ on the intensity of the resonance can be counterbalanced by the prefactor $P = C \cdot \rho_s / \pi$ (see Eq. 1 of the main text). Hence an increase in the prefactor can be compensated with a decrease in $r_{l,r}$. This can lead to ill-determined reflection coefficients in our fit. However relative values, measured as the asymmetry factor $R_{as} = (r_l - r_r)/(r_l + r_r)$, are robust, since they are mainly sensitive to the relative intensities of the wave function maxima, which are accessible for N = 2. The above problem does not affect the phase shifts, since these depend on lateral shifts of the maxima and not on their intensity.



FIG. S4. Fit parameters obtained for varying prefactor P for the two types of resonator. The green line indicates the value obtained in the fit with $P = C \cdot \rho_s / \pi$ as free parameter.

In order to check the robustness of our fitting results, we have preformed a series of fits where the prefactor P was varied around the value of the initial free fit [Table I of the main text, corresponding to solid lines in Fig. 4(b)]. In the case of A type resonators, the free fit already resulted in the upper limit value of $r_l = 1$, therefore P was only varied towards increasing values, leading to decreasing r_l . For B type resonators the prefactor was varied in the two directions. In both cases we covered changes in P by a factor of three. The results are displayed in Fig. S4. Despite the significant variation of the reflection coefficients, we find that variations of R_{as} remain moderate, 12% and 17% for A and B type resonators respectively. The effect on the phase is negligible (< 3%). Thus we can say that the differences in phase and reflection asymmetry between the two type of resonators obtained from the fit are reliable and related to the different scattering properties of each resonator.

V. LATERAL SHIFT OF RESONANCES

The lateral shift between wavefunctions of occupied and and unoccupied resonances does not only occur for N = 2, as shown in Fig.4(b), but is a general feature. This can be directly appreciated in the series of spectra shown in Fig. S1, where the spatial distribution of all resonances is simultaneously resolved. In this plot one can note that all resonances of the unoccupied band are well aligned with the center of the resonator, indicated with an orange vertical line. In contrast, the N = 1 and N = 2resonances that can be distinguished of the occupied band are clearly shifted to the right.

In order to check if the observed lateral shift between the N = 2 resonances of occupied and unoccupied bands is only related to their different spatial localization and does not depend on the resonance level, we performed for N = 1 a similar analysis as that shown for N = 2 in Fig.4(b). The main conclusion can be readily obtained by just comparing the resonances of the two type of resonators, shown in Fig. S5. As for N = 2, resonances for *B* type resonators are both centered at the terrace, whereas for *A* type resonators, the occupied resonance is shifted to the right. The relative shift is quantified by fitting the data with gaussian functions to determine the center of the wavefunctions. The resulting shift of 5.9 Å, is close to that observed for the N = 2resonances.



FIG. S5. dI/dV(x) for the N = 1 resonance of the unoccupied (closed symbols) and occupied band (open symbols) for A (left) and B (right) type resonators (L = 70 Å and 75 Å respectively). The center of the terrace (x_c) and step edges are indicated by black and green vertical dashed lines respectively. Resonances in A type resonators show a clear relative shift (Δ), whereas those in B type resonators are centered with respect to step edges.

We further performed ab-initio calculations to support the observed experimental shifts in the lateral confinement. For the simulation we restrict ourselves to a single layer of Ag(111) covered with a BiAg₂ surface alloy. The band structure [Fig. S6(a)] shows all characteristic features observed in the thicker systems, in particular the (s,p_z) -states around and below the Fermi level and the $m_j = 1/2$ states reaching up to 0.8 eV in this case, forming respectively the occupied and unoccupied bands addressed in the main text. We cut out a ribbon of the surface alloy layer, about 25 Å wide [Figs. S6(b) and (c)], showing an A type step terminated with a Bi row on the left and two Ag rows at the right side. With this structural setup, we study the evolution of the density of states in different energy windows. Two examples, one window in the unoccupied states around 0.4 eV and one in the occupied states below the Fermi level are shown in Figs.S6(b) and (c), respectively. In (c) the states are more Ag localized and the (s,p_z) character at the Bi atoms is clearly visible. If we compare to panel (b) two changes are observed: At higher energies the charge density at the position of Ag atoms at the right edge of the ribbon gets smeared out. Weight is transferred from the

Ag to the Bi states, that change their character from (s,p_z) to (p_x,p_y) type. These results demonstrate that the observed shift between occupied and unoccupied resonances in A type resonators is related to their different localization on the BiAg₂ plane. Further, the overall shift towards the left is observed as a shift outward the resonator in Bi-terminated steps, and inward the resonator in Ag-terminated ones. Comparing that to the experimentally observed shift, we can conclude that A type resonators are Bi-terminated.



FIG. S6. (a) Spin-resolved band structure calculated for a single layer of Ag(111) covered with a $BiAg_2$ surface alloy. Resonators are simulated with finite stripes of the $BiAg_2$ layer. An schematic is shown in (b) and (c), where Bi(Ag) is represented with green (white) balls. The LDOS(x) integrated in an energy range around the unoccupied (b) and the occupied (c) bands is superimposed in greyscale.

VI. BAND STRUCTURE CALCULATIONS

The orbital and spin composition of the band structure along the ΓK and ΓM directions are shown in Figs. S7(a) and (b) respectively. They exhibit identical composition, but with p_x^{\pm} and p_y^{\mp} interchanged.



FIG. S7. Orbital and spin-resolved band structure along the ΓK (top) and ΓM (bottom) directions. The size of the symbols indicates the Bi p_z (left) p_x (middle) and p_y (right) contribution to the state. Opposite spin directions are shown by full and empty symbols.