



Splitting of Shockley surface states in thin films of noble metals

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ABSTRACT

The splitting of the surface bands of Cu(1 1 1), Ag(1 1 1), and Au(1 1 1) films is studied by means of relativistic density-functional theory (DFT) calculations. It is found that the splitting of the bands of clean films obtained in semirelativistic approximation, in agreement with previous studies, stems from the interaction between the surfaces and hence depends on the thickness of the slabs. Since the Kramers' degeneracy is not broken by the presence of the surface, the spin-orbit coupling does not lead to the spin-splitting of the bands. An H monolayer, deposited on one face of the film, breaks the inversion symmetry and results in the appearance of the Rashba-type splitting of the bands.

1. Introduction

It was believed for a long time that the band structure of a noble metal may be considered as having a relative gap for certain directions in the Brillouin zone (BZ) and hence for related directions in real space. This is just the case for the $\langle 111 \rangle$ direction, and therefore the (1 1 1) surface might behave like a semiconducting one. The twin surface states crossing E_F (actually, bands with strong surface weights, that is, rigorously speaking, surface resonance bands) with a parabolic dispersion, pertinent to nearly free electrons, were found in angle-resolved photoemission studies for Au(1 1 1) [1–5], Ag(1 1 1) [2,5], and Cu(1 1 1) [6]. Quite naturally, these states, by analogous with similar states in semiconductors, were called Shockley surface states.

It was a very attractive idea then to apply the theory of a two-dimensional (2D) electron gas to these surfaces. In particular, the twinning of the surface bands of Au(1 1 1) surface and films was attributed to spin-orbit coupling due to its apparent similarity with the spin-splitting of bands that appears in the Rashba theory of a 2D electron gas [7–12]. However, the degree of localization of the wave function of electrons in surface states of Au(1 1 1) is obviously quite different from that needed to make the 2D theory relevant at least qualitatively. This deficiency becomes obvious when the energy split of the Au(1 1 1) surface bands is compared with the estimates obtained from the theory. Indeed, the disagreement of approximately six orders in magnitude [2–4] hardly could be considered as acceptable. Nonetheless, the conclusions derived from application of the theory to the Au(1 1 1) surface bands were suggested to be qualitatively correct [1–5]. Probably, this interpretation, in large part, was inspired by a rapidly growing interest to so-called topological insulators [13–16] and, in this regard, to apparent perspectives for creation of spin-separating surfaces based on

quantum spin-Hall effect [16].

In the 2D electron gas, Rashba splitting leads to the spin polarization of the bands within the surface plane. Accordingly, the twin Au(1 1 1) surface states must show an opposite spin polarization, which has been reported in a number of spin- and angle-resolved photoelectron spectroscopy studies of this and similar Ag(1 1 1) and Cu(1 1 1) surfaces [1–6,9–11]. It should be mentioned, however, that the interpretation of spin-resolved photoemission spectra can become complicated due to the various spin-polarization effects [3].

The interpretation of the splitting of the surface bands as a Rashba-type splitting was supported by tight-binding calculations [1,8], which were not finally persuasive because of presence of adjustable parameters, so that an apparently stronger confirmation of the theory was obtained later from relativistic first-principles calculations for Au(1 1 1) slabs [2]. However, for the slabs, the twinning of the surface bands appears already in semirelativistic calculations, that is, without account for spin-orbit coupling (SOC). This means that the splitting of the bands, observed in experiments, does not have to be originated from relativistic effects but, rather, can be explained by some interactions between opposite surfaces (or interfaces) of the films.

The inversion symmetry of a crystal, $E(-\mathbf{k}, \uparrow) = E(\mathbf{k}, \uparrow)$ together with the time-reversal symmetry $E(-\mathbf{k}, \uparrow) = E(\mathbf{k}, \downarrow)$ leads to $E(\mathbf{k}, \uparrow) = E(\mathbf{k}, \downarrow)$, that is, to the Kramers' spin-degeneracy of the bands for all \mathbf{k} apart of some high-symmetry points of Brillouin zone, such as Γ and M for the Au(1 1 1). Hence, the lifting of the Kramers' degeneracy of bands in the absence of current requires the break of the inversion symmetry, which in the case of Au(1 1 1) was suggested to be produced just by the surface itself, specifically, by the surface potential barrier [1–3,9–12].

The concept of the break of inversion symmetry by the presence of a surface, however, has an obvious deficiency. Indeed, any surface cannot

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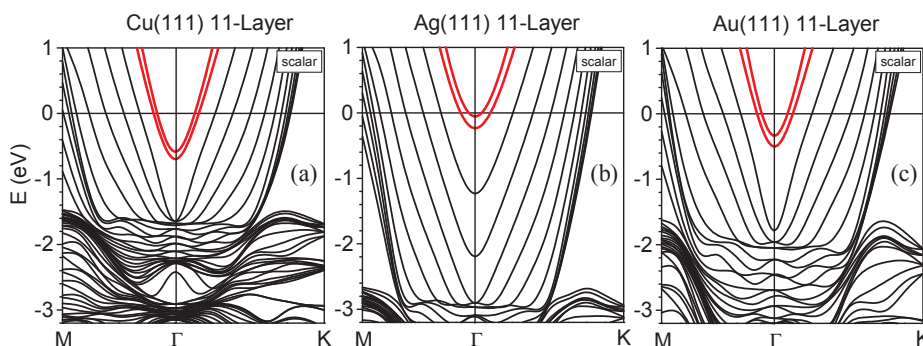


Fig. 1. The band structures of Cu(1 1 1) (a), Ag(1 1 1) (b), and Au(1 1 1) (c).

be separated from the bulk, and therefore cannot have its own symmetry different from the symmetry of the net system. It should be noted also that any real crystal or film always has an opposite surface, which restores the inversion symmetry, while all experiments are performed either for films adsorbed on appropriate substrates or for surfaces with some unavoidable defects and contaminations and hence, because of biased determination of the spin polarization and actual surface conditions, could be interpreted differently. In calculations using the supercell (repeated-slab) model, the break of the symmetry can be effected, for example, by H monolayer adsorbed on one face of the film, but for clean surfaces the slabs will hold the inversion symmetry.

In the present paper the twin surface bands of the Au(1 1 1), Ag(1 1 1), and Cu(1 1 1) surfaces are studied by means of density-functional theory (DFT) calculations using the repeated-slab model both in scalar relativistic and full-relativistic approximations, that is, without and with account for spin-orbit coupling (SOC), respectively. This approach allows for revealing the role of SOC in the splitting of surface bands by comparing obtained band structures.

2. Methodology

The calculations were performed using the plane-wave decomposition of the wave functions with ABINIT [17] set of programs. The electronic structure of the surfaces was computed using the supercell (repeated slab) model. The local density approximation (LDA) exchange-correlation potential was taken in the Goedecker-Teter-Hutter (GTH) form [18]. With chosen Troullier-Martins [19] pseudopotentials, the cutoff energy of 24 Ha and $6 \times 6 \times 1$ lattice of k -points provided the 0.001 Ha convergence of the energy. The slabs were built from (1 1 1) planes of the fcc crystals (which also could be viewed as being cut from the crystals parallel to (1 1 1) planes) and then their structures were optimized within a semirelativistic (scalar) approximation using standard Broyden method. The structural optimization was performed in all cases until the forces on atoms became below $0.05 \text{ eV}/\text{\AA}$, which allowed for the determination of atomic positions with accuracy of $\sim 0.02 \text{ \AA}$. The quality of chosen pseudopotentials was further verified by means of calculations of lattice constants of equilibrated bulk structures. For example, the estimated lattice period a for Au was found to be of 4.10 \AA , which is consistent with the experimental value 4.08 \AA . For Ag, estimated period is $a = 4.07 \text{ \AA}$ (experimental value is 4.09 \AA), and for Cu $a = 3.59 \text{ \AA}$ (experimental value is 3.61 \AA). The band structures of bulk Ag and Ag(1 1 1) slabs were additionally verified using another type of pseudopotential, specifically, Hartwigsen-Goedecker-Hutter (HGH) [20], which is standard in ABINIT. These test calculations gave the bands which coincided with the bands calculated using Troullier-Martins pseudopotentials.

It is well known that some important details of band structures, calculated in the supercell geometry, depend on the thickness of the slab and, to a minor extent, on the width of the vacuum gap, provided that this width is sufficient to neglect remaining interactions between the neighboring slabs. For example, in [2], the vacuum gap was

adopted to be of 20 Bohr, that is, 10.6 \AA . The vacuum gaps between Au, Ag, and Cu slabs in the present study were about $10\text{--}16 \text{ \AA}$, and it was verified that a further increase of the gaps did not lead to any noticeable changes in calculated band structures.

Surface states/resonances can be identified by significant weights of wave functions at surface atoms, which can be characterized by a relative electronic charge of two outermost surface layers. In the present study, the surface states are defined as those having more than 50% localization at surfaces (similar criterion was adopted in Ref. [2]).

In ABINIT, plane wave full-relativistic calculations are performed by solving Dirac equations thus obtaining electronic wave functions in the vector form of two-component spinors. In semirelativistic calculations, all relativistic corrections (including Darwin term) are accounted for, so that the band structures obtained in scalar and vector calculations differ only by SOC, which allows one to directly compare the surface bands to reveal the role of SOC.

3. Results

The surface band structures, calculated for 11-layer Cu(1 1 1), Ag(1 1 1), and Au(1 1 1) slabs in a scalar relativistic approximation, are shown in Fig. 1. Surface bands (that is, the bands of states with substantial surface weights), marked red in the Fig. 1, have a nearly parabolic shape in vicinity of Γ point, pertinent to Shockley surface states. The most interesting and unusual property of these bands is a well pronounced splitting, which may be characterized as a twinning of the bands. It should be noted that this splitting of the surface bands is not a result of SOC, since it appears already in a scalar relativistic approximation. Furthermore, the bands are shifted in energy (not in \mathbf{k}), so they are parallel to each other thus having a gap also at Γ point, which is absent for a Rashba-type splitting.

It is seen in Fig. 1 that the band structure in the case of Ag(1 1 1) is significantly different from Cu(1 1 1) and Au(1 1 1), which is somewhat unusual because of Ag position between Cu and Au in the Periodic Table. For Ag(1 1 1), the main part of d -band lies much lower (with respect to E_F) than for Cu(1 1 1) and Au(1 1 1) and, the most important, the surface bands lie significantly higher, so the upper surface band crosses E_F only in vicinity of Γ (Fig. 1b).

The dependence of the splitting of the surface bands of Au(1 1 1) on the thickness of slabs was studied earlier by means of DFT calculations [2,21]. In particular, it was shown that the splitting decreases with increasing thickness (down to 0.01 eV for a 23-layer Au(1 1 1) [2,21]), which was attributed to interaction between surface states [2]. For Ag(1 1 1), the transformation of the bands with increasing thickness of the slabs is found to be very similar (Fig. 2).

It should be noted in this regard that, rigorously speaking, any states cannot interact because they are not material objects. In the case of relatively thick Ag(1 1 1) slabs (or Au(1 1 1) slabs in Ref. [2]) one might assume that this terminology implies the interaction between electrons in these surface states, but this assumption fails for thinner Ag(1 1 1)

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