Termination dependence of the surface states in Pb$_2$Pd

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Topological properties of systems lead to the emergence of surface states which can be observed experimentally within the angle-resolved photoemission spectroscopy (ARPES) measurements. Recently, the topological properties of Pb$_2$Pd were reported. In this paper, we discuss the role of the surface termination on the realized surface states. We discuss the termination dependence of the surface state for (001) and (110) surface. We demonstrate that the Pd terminated (001) surface allow realization of the Dirac cone-like surface state. In the case (110) we observe well visible surface states with parabolic-like dispersion relation in close vicinity of the Fermi level.

I. INTRODUCTION

The surface states and their topological behaviors were intensively investigated in past years [1, 2]. Best example of such states are the “metallic” surface states observed experimentally within the angle-resolved photoemission spectroscopy (ARPES) in the topological insulators [3–5]. The topological surface states preserve theirs properties also in presence of the magnetic impurities [6–8], and that in the presence of intrinsic magnetism can be source of new classes of magnetic topological insulators [9–12]. More recently, realization of the Dirac [13–15], Weyl [16–20], or nodal line [21–27] semimetals have drawn a lot of attention too.

Metalic systems can also exhibit the topological properties. One such example is Pb$_2$Pd, which was first recognized as a superconductor in 1962 [28]. Powder XRD measurements confirm realization of the I4/mcm space group [29]. System remained the same after Bi-doping and the cell volume monotonically increased with higher Bi content [30]. Similarly to PdT$_e_2$ [31], Pb$_2$Pd exhibit conventional s-wave superconducting behavior of the specific heat jump at $T_c$ around 3 K [28, 29, 32].

Independent of the realized symmetry, the Pd-terminated Pb$_2$Bi$_2$ compounds (like PdAu$_2$ [33], PdSb$_2$ [34], PdT$_e_2$ [35–38], or PdBi$_2$ [39, 40]) typically exhibit topological properties.

For example, in case of PdT$_e_2$ (with P3m1 symmetry) the bulk Dirac point and topological surface states were reported [35–38]. Initial theoretical results also suggest topological properties in the case of Pb$_2$Pd [29], however, this feature is yet to be studied properly. In this paper, we discuss the electronic properties of Pb$_2$Pd (electronic bulk band structure, and termination dependence of the surface states). This paper is organized as follows. In Sec. II we present and discuss our numerical results, which are concluded in Sec. III.

II. NUMERICAL RESULTS AND DISCUSSION

A. Calculations details

The first-principle calculations were performed within density-functional theory (DFT) using the projector augmented-wave (PAW) method [41] implemented in the Vienna Ab initio Simulation Package (VASP) [42–44]. The exchange-correlation potential was obtained by the generalized gradient approximation (GGA) in the form proposed by Perdew, Burke, and Enzerhof (PBE) [45]. The energy cut-off for the plane-wave expansion was equal to 400 eV. The optimization of the conventional cell was performed using a $12 \times 12 \times 12$ Monkhorst-Pack $k$-grid [46].

The structures were relaxed using the conjugate gradient technique with the energy convergence criteria set at $10^{-8}$ eV and $10^{-6}$ eV for the electronic and ionic iterations, respectively. Symmetry of the structures were analyzed with FINDSYM [47] and SEEK-PATH [48, 49] packages.

Using results of the DFT calculation for electronic band structure we can find the tight binding model in the basis of the maximally localized Wannier orbitals [50–52]. It can be performed via the WANNIER90 software [53–55]. In our calculations, we used the $10 \times 10 \times 10$ full $k$-point DFT calculation, starting from $p$ orbitals for Pb atoms, $p$ and $d$ orbitals for Pd atoms. This gives us $28$-orbital tight binding model of the Pb$_2$Pd. Finally, to study the surface states, the surface Green’s function for semi-infinite system [56] was calculated using WANNIERTOOLS [57].

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FIG. 1. Crystal structure of Pb$_2$Pd with I4/mcm symmetry (left), and the corresponding Brillouin zone with their high symmetry points (right).
B. Crystal structure

\( \text{Pb}_2\text{Pd} \) crystallize with \textit{I}4/mcm symmetry (space group No. 140), i.e. a body-centered tetragonal unit cell with Pd atoms at the body center. After the DFT optimization, the lattice constants were found to be \( a = b = 6.997 \text{ Å}, \) and \( c = 5.920 \text{ Å} \), which are close to the experimentally reported values \( a = b = 6.863 \text{ Å}, \) and \( c = 5.840 \text{ Å} \) \[29\]. The Pd and Pb atoms are located in the high symmetry Wyckoff positions \( 4a \) \((0,0,0.25)\), and \( 8h \) \((0.1630,0.6630,0)\), respectively. Here it should be noted that the experimentally obtained Pb atom position was \((0.1643,0.6643,0)\), which is close to the theoretical one \[29\].

C. Bulk electronic band structure

The bulk electronic band structure is presented in Fig. 2 (orange and blue lines correspond to the results in the absence and presence of the spin–orbit coupling, respectively). In the band structure, several nearly-flat bands (approximately 2 eV below the Fermi level) can be distinguished. However, around the Fermi level, the bands exhibit strong dispersion.

This spin–orbit coupling lead to lift the band degeneracy. This is well visible, e.g., at the \( \Gamma \) point, where splitting is in range of 0.5 eV. However, largest impact of the spin–orbit coupling on the band structure is visible mostly above the Fermi level – e.g. at M point, around 2 eV above the Fermi level, where the strong band structure is observed.

Four bands forming the Fermi surface (Fig. 3) have electronic character. First two bands, with nearly parabolic-like dispersion relation around \( \Gamma \) point, create two sphere-like pockets [Fig. 3(c) and (d)]. Next two

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**FIG. 2.** Bulk electronic band structure of \( \text{Pb}_2\text{Pd} \) with \textit{I}4/mcm symmetry. The orange and blue line show results in the absence and presence of the spin–orbit coupling, respectively.

**FIG. 3.** The Fermi surface of \( \text{Pb}_2\text{Pd} \) with \textit{I}4/mcm symmetry, in the presence of the spin–orbit coupling. Panels (a) and (b) present the full Fermi surface, while panels (c)–(f) present the separate pockets.
bands present strong $k$-dependence [Fig. 3(e) and (f)].

**D. Surface states**

Now, we will present analyses of the surface states for (001) and (110) surfaces (Fig. 4 and Fig. 5, respectively), which hosts the surface states in close vicinity of the Fermi level.

The electronic band structure calculated for the slab geometry [panels (b)] presents a very complex structure [blue to the projection of the 3D bulk Brillouin zone to 2D surface Brillouin zone, presented in panels (a)]. Absence of periodic boundary conditions along the direction parallel to the surface allow realization of the surface states as a consequence dangling bonds of the atoms on the surface. Indeed, direct analyses of the band projection on the surface atoms reflects the presence of the surface states [color contours on panels (b)]. The realized geometry allows us to find the surface states realized by the surface terminated by the Pb atoms (blue color), as well as by the Pd atoms (red color). As we can see, in case of the (001) surface [Fig. 4(b)], the Dirac cone-like structure at the $X$ point is well visible. In the presented range of energies around the Fermi level we do not observe any surface states coming from the Pb terminated surface. Contrary to this, for the surface (110), both the terminated surfaces allow the realization of the surface states. Here we can distinguish several surface states in close vicinity of the Fermi level (from both type of terminations).

We also calculate the surface Green’s function (spectral function) for semi-infinite system with Pb and Pd termination [panels (c) and (d) on Fig. 4 and Fig. 5, respectively]. In the case of the Pb terminated (110) surface, the surface state form parabolic-like band crossing the Fermi level [marked by green dashed line in Fig. 5(c)]. However, also for deeper energies the surface states are visible as separate sharp lines with high spectral weights (marked by black arrows around $-1.5$ eV in Fig. 5(c)).

In the case of Pd termination of (001) surface, the earlier mentioned Dirac cone-like structures are also well visible in the spectral function [marked by black arrows in Fig. 4(d)]. For (110) surface, the surface states coming from Pd termination are better visible for several energies at $N$ point. Firstly, the parabolic like surface states crossing the Fermi level. Also two separated surface states at 0.5 eV and $-1.25$ eV are visible [marked by the black arrows in Fig. 5(d)].

As we mentioned above, in the case of the (110) surface, the parabolic-like surface states are well visible in the spectrum. Here it is worth mentioning that this parabolic dispersion relations have different character for Pb termination (electron like) and for Pd termination (hole like).
III. SUMMARY

In summary, we discussed the surface states realized in the Pb$_2$Pd, for (001) and (110) surfaces terminated by Pb or Pd atoms. As a consequence of dangling bonds of the atoms at the surface, the electronic surface states can be realized. We calculate the surface Green’s (spectral) functions for the mentioned surfaces. In the case of the (001) surface, the Dirac cone surface states at the $\bar{X}$ point can be observed. However this surface state is located deep down the Fermi surface, and should not play an important role in the physical properties of the Pb$_2$Pd. Contrary to this, for (110) surface, the surface states can be realized for both termination of the surface. Additionally, the surface states around $\bar{N}$ point, exist in close vicinity of the Fermi surface. Moreover, this states exhibit parabolic-like relation with different (electron- or hole-like) character. In our opinion, such states should be observed experimentally in a relatively simple way within the ARPES measurements.

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