Defect-controlled Fermi-level tuning in half-Heusler topological semimetals

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Three-dimensional topological semimetals host a range of interesting quantum phenomena related to band crossing and band touching that give rise to Dirac or Weyl fermions, and could be engineered into novel technological applications. Harvesting the full potential of these materials in applications will depend on our ability to position the Fermi level near the symmetry-protected band crossings or touchings so that exotic spin and charge transport properties are manifest. Using first-principles calculations based on density functional theory, we investigate how point defects impact the Fermi level position in two representative half-Heusler topological semimetals, PtLuSb and PtLuBi; we explore how intrinsic defects can be used to tune the Fermi level, and explain recent observations based on Hall measurements in bulk and thin films. Under typical growth conditions we show that Pt vacancies are the most abundant intrinsic defects, leading to excess hole densities that place the Fermi level significantly below the expected position in the pristine material. Suggestions for tuning the Fermi level by tuning chemical potentials are discussed.

I. INTRODUCTION

Half-Heusler (h-H) compounds form a class of ternary intermetallics with diverse electrical and magnetic properties, that includes semiconductors [1], semimetals [2], half-metals [3, 4], and topological semimetals [5–7]. Having a structure that can be viewed as zinc-blende with filled tetrahedral interstitial sites with robust chemical flexibility for occupying the three nonequivalent sites allows for tuning these properties over wide ranges. Recent reports on h-H semimetals with band structures featuring non-trivial topology, such as in PtLuSb [6, 8, 9] and PtLuBi [7, 10, 11], generated great interest in exploring charge and spin transport properties of these materials for novel technological applications. In general, topological semimetals are classified as Dirac, Weyl, or node-line semimetals, characterized by symmetry-protected surface states with the presence of band touching points (and Dirac cones), where two or more bands are exactly degenerate at particular values of the crystal momentum in the first Brillouin zone, or line nodes, where bands are degenerate along closed lines in momentum space. Having the Fermi level placed at or sufficiently close to these topological features is key to the observation and utilization of the exotic topological properties in devices. More often than not, these features are either buried deep in the occupied valence bands or too high together with empty conduction bands relative to the Fermi level.

Therefore, finding ways to tune the Fermi level, by adding impurities (doping) or deliberately introducing intrinsic defects that minimally perturb the underlying topological band structure, is crucial for harvesting the full potential of these interesting class of materials.

In the case of PtLuSb and PtLuBi, Hall measurements [6, 10] show hole conductivity with sizeable hole densities of $3 \times 10^{20}$ cm$^{-3}$ and $2 \times 10^{19}$ cm$^{-3}$, indicating that the Fermi level lies well below what one would expect for the ideal perfect crystal (as discussed later), and angle-resolved photoelectron spectroscopy (ARPES) indicate a Fermi level well below the Dirac point of the topological

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surface states in LuPtSb [6], and well above the Dirac point in LuPtBi [7]. The origin of the extra bulk carriers, if intrinsic defects or impurities, is still unknown. Using first-principles calculations based on the density functional theory we investigate the impact of intrinsic defects and impurities on the Fermi level position with respect to that expected in perfect crystalline material, searching for an explanation for the observed extra holes and Fermi level position in these materials. We also lay out design principles to tune the Fermi level by adding specific impurities or changing the atomic chemical potentials during growth to control the concentration of specific intrinsic defects that strongly affect the Fermi level position in the desired direction. We find that the presence of Pt vacancies in both PtLuSb and PtLuBi can explain the observed hole carrier densities and discuss how this effect can be reversed and the Fermi level controlled by adding impurities.

The calculations of intrinsic defects in the topological semimetals PtLuSb and PtLuBi are based on the density functional theory [12, 13] within the generalized gradient approximation [14] and the projector augmented wave (PAW) potentials [15] as implemented in the VASP code[16, 17]. Equilibrium lattice parameters and band structures were calculated using the primitive cell containing three atoms, with a 16×16×16 Γ-centered mesh of k points for the integrations over the Brillouin zone. For the defect calculations, we used a cubic supercell containing 96 atoms which corresponds to a 2×2×2 repetition of the conventional 12-atom cubic unit cell of LuPtSb(Bi), with Γ-centered 4×4×4 mesh of special k points. All calculations were performed using a kinetic-energy cutoff of 400 eV for the plane-wave basis set. The 4f electrons of Lu, that form completely occupied bands, were considered as core electrons. Previous calculations of band structures of LuSb and LuBi show that the occupied 4f bands are well below the Fermi level (by more than 8 eV), in agreement with photoelectron spectroscopy measurements in LuPtBi [7], and do not affect the structural properties or electronic band structure near the Fermi level [18]. The effects of spin-orbit coupling are included in all calculations.

The structure of half-Heusler compounds ABC (A= Lu; B= Pt; C= Sb or Bi) can be visualized as three interpenetrating fcc lattices described by a primitive cell containing three atoms, with the atomic positions (0.5,0.5,0.5)a, (0.25,0.25,0.25)a and (0,0,0) for A, B and C respectively, where a is the lattice parameter. Thus, Lu and Sb(Bi) form a rock salt structure while Pt and Sb form a zinc blende structure, as shown in Fig. 1. The calculated lattice parameters for LuPtSb and LuPtBi are 6.443 Å and 6.572 Å, in good agreement with the experimental values of 6.457 Å and 6.578 Å [6, 9, 10].

The electronic behavior of half-Heusler compounds is closely related to the number of valence electrons [19]. These compounds exhibit semiconducting properties similar to that of conventional semiconductor GaAs when the total number of valence electrons per formula unit is equal to 8 or 18 (closed shell), following the 8 or 18 electron rule. To understand the topological properties
in semimetallic members of this family, represented here by LuPtSb and LuPtBi, the band structure of HgTe can serve as a starting point. HgTe is a well known topological semimetal with a band inversion between Hg-6s state ($\Gamma_6$) and Te-p state ($\Gamma_8$) at the $\Gamma$ point. The Fermi level in the intrinsic material is located at the point where conduction band touches the valence band at $\Gamma$. Similar band inversion occurs in LuPtSb and LuPtBi, as displayed in the orbital-resolved electronic band structure shown in Fig. 2(a-f). For LuPtSb the occupied bands near the Fermi level originate mostly from the Sb atom, with the inversion between $\Gamma_8$ ($p$-character) and $\Gamma_6$ ($s$-character) making it a compensated semimetal with a topologically non-trivial band structure (Fig. 2(c)], in agreement with previous studies[6, 8, 20]. The Lu-5d orbitals mostly contribute to the bands 2-4 eV above the Fermi level, whereas Pt-5d occupied bands are around 4 eV below the Fermi level. The calculated band inversion strength (BIS) for LuPtSb is 0.23 eV, in agreement with previous studies[6, 8, 20]. The band structure of LuPtBi is qualitatively similar, with the $\Gamma_8$ state well above the $\Gamma_6$ state, as shown in Fig. 2(d-f), also in agreement with the previous studies[8, 20]. The calculated band inversion strength (BIS) for LuPtBi is 1.55 eV, being significantly larger than in LuPtSb due to the stronger spin-orbit coupling.

Defects are modelled by removing, adding, or replacing an atom in a supercell using periodic boundary conditions. The results of defect calculations reported here are obtained using a supercell with 96 host atoms, and convergence tests for the lowest energy defects using supercells of 324 and 768 atoms, show that formation energies change by less than 0.05 eV, and do not change our conclusions. The formation energy for a defect $X$ is given by:

$$E^f[X] = E_{tot}[X] - E_{tot}[host] + n_i \sum_i (E_{tot}[X_i] + \mu_i),$$ \hspace{1cm} (1)

where $E_{tot}[X]$ is the total energy of the supercell containing the defect $X$, $E_{tot}[host]$ is the total energy of the perfect crystalline host material using the same supercell, $n_i$ is the number of atoms that are removed/added to the supercell to form the defect $X$, and $\mu_i$ is the atomic chemical potential, i.e., the energy of the atomic reservoir for the species added/removed, referenced to the total energy of the respective elemental phases $E_{tot}[X_i]$, and can be related to the experimental growth or processing conditions. The chemical potentials $\mu_i$ are not free parameters, but are bound to the stability condition of the host material (LuPtSb or LuPtBi, in this case) and the need to avoid the formation of possible secondary phases, such as LuSb, LuPt, PtSb2, and LuPt3, in the case of LuPtSb, through the following relations:

$$\mu_{Lu} + \mu_{Pt} + \mu_{Sb} = \Delta H^f[LuPtSb],$$ \hspace{1cm} (2)

$$\mu_{Lu} + \mu_{Sb} < \Delta H^f[LuSb],$$ \hspace{1cm} (3)

$$\mu_{Lu} + \mu_{Pt} < \Delta H^f[LuPt],$$ \hspace{1cm} (4)

$$\mu_{Pt} + 2\mu_{Sb} < \Delta H^f[PtSb2],$$ \hspace{1cm} (5)

$$\mu_{Lu} + 3\mu_{Pt} < \Delta H^f[LuPt3],$$ \hspace{1cm} (6)

with $\mu_{Lu} \leq 0$, $\mu_{Pt} \leq 0$, and $\mu_{Sb} \leq 0$ representing the upper limits set by the respective elemental phases. Similar equations are considered for LuPtBi. The range of chemical potentials in the plane $\mu_{Lu}$ vs $\mu_{Pt}$ for LuPtSb and LuPtBi are shown in Fig. 3, where the relevant regions for the discussion are indicated. The calculated formation energies of all the native point defects, i.e., vacancies, interstitials, and antisites, on the three sublattices in LuPtSb and LuPtBi are listed in Table I and Table II for points A, B, C, and D indicated in the diagrams of Fig. 3.

The accessible atomic chemical potential region for LuPtSb is relatively larger than for LuPtBi. In the phase stability diagram of LuPtSb, we see that $V_{Pt}$ is the lowest formation energy defect along the line bordering the formation of LuSb (segment 4) in Fig. 3(a), from Sb-rich to Lu-rich (point B), whereas $V_{Pt}$ has the highest formation energy equal to 6.451 eV. The formation energy of LuSb at point A, also corresponding to Sb-rich limit, is slightly higher (0.635 eV) The formation energies for all the point defects are found to be greater than 1 eV at point C and D. Overall, we predict that $V_{Pt}$ is the

| Defect | Formation energy (eV) |
|--------|-----------------------|
| $Sb_{Lu}$ | 1.096 | 3.281 | 2.607 | 1.097 |
| $Sb_{Pt}$ | 4.452 | 5.438 | 6.112 | 5.810 |
| $Pt_{Lu}$ | 4.090 | 5.289 | 3.942 | 2.733 |
| $Pt_{Sb}$ | 3.500 | 2.514 | 1.841 | 2.143 |
| $Lu_{Sb}$ | 4.075 | 1.890 | 2.564 | 4.074 |
| $Lu_{Pt}$ | 6.451 | 5.252 | 6.600 | 7.809 |
| $Sb_{i}$ | 4.501 | 5.558 | 5.558 | 4.953 |
| $Pt_{i}$ | 2.975 | 3.046 | 2.372 | 2.070 |
| $Lu_{i}$ | 5.048 | 3.920 | 4.594 | 5.500 |
| $V_{Lu}$ | 1.914 | 3.042 | 2.368 | 1.462 |
| $V_{Pt}$ | 0.635 | 0.564 | 1.238 | 1.540 |
| $V_{Sb}$ | 4.148 | 3.091 | 3.091 | 3.696 |
most likely defect to form in LuPtSb, corresponding to $\mu_{Lu} = -2.0 \text{ eV}$, $\mu_{Pt} = -1.5 \text{ eV}$, and $\mu_{Sb} = 0 \text{ eV}$ (Sb-rich limit) near the point A.

In case of LuPtBi, the stability region [Fig. 3(b)] is relatively smaller yet the results are qualitative similar to those of LuPtSb. In the region close to point C, all the point defects have formation energies greater than 1 eV. The Pt vacancy is the lowest energy defect with formation energy equal $E_f = 0.592 \text{ eV}$, as listed in Table II. Moving along the Bi-rich line toward the Lu poor region, we find Bi$_{Lu}$ to be another point defect with the lowest formation energy of $E_f = 0.568 \text{ eV}$. So, for chemical potentials near the Bi-rich and Pt-poor lines (near the LuBi phase), the lowest energy defect is by far the Pt vacancy, as in LuPtSb.

Experimentally, thin-film growth of LuPtSb by molecular beam epitaxy (MBE) [6, 9] or bulk growth of LuPtBi [11, 21] were carried out in Sb/Bi-rich environments, and were most likely to happen near point A in the stability diagrams of Fig. 3.

Given the prevalence of the Pt vacancy as the defect of low formation energy in large part of the stability phase diagram of LuPtSb and LuPtBi, and, in particular, near the region where growth were carried out, we expect it to play major role in determining the electronic characteristics of the reported bulk and thin films. Considering that Pt and Sb compose a zinc blende sublattice within LuPtSb, removing a Pt atom leads to Sb dangling bonds, and according to the electronic band structures in Fig. 2, we expect Sb dangling bonds to introduce partially occupied bands near the Sb-related $5p$ bands just below the Fermi level, and lead to excess hole carriers, i.e., a predominant $p$-type behavior, compared to the compensated pristine perfect material where electron and hole concentrations are the same. Similarly, Pt vacancies in LuPtBi would also lead excess holes. This is consistent with the behavior of Pt vacancies in half-Heusler semiconductors, which were predicted to act as acceptors [22]. Thus, our results are also consistent with the experimental observations in LuPtSb [6, 9], and LuPtBi [11, 21], where excess holes have been observed in thin films and bulk single crystals grown or deposited under Sb- and Bi-rich conditions.

Each Pt vacancy in LuPtSb and LuPtBi is then expected to result in three holes, taking the oxidation state $\text{Sb}^{3+}$ in the pristine materials. Assuming that the measured hole concentrations in LuPtSb and LuPtBi, of 2-3x10$^{20}$ cm$^{-3}$, [6, 9] and 2-4x10$^{19}$ cm$^{-3}$ [11, 21], determined from Hall measurements, originate from Pt vacancies incorporated during growth at temperatures in

![FIG. 3. (color online) The allowed chemical potential region (yellow shading) in $\mu_{Lu}$ versus $\mu_{Pt}$ plane along with some of the other competing phases for (a) LuPtSb and (b) LuPtBi.](image-url)
the range $T=450^\circ$C (thin films) to $T=800^\circ$C, we can invert the equation for the concentration of Pt vacancies ($c = N_{\text{sites}} \exp(-E_f/k_B T))$, where $N_{\text{sites}}$ is the number of sites per cubic centimeter that the vacancy can be incorporated on) to obtain vacancy formation energies of 0.375 eV for LuPtSb (taking from thin-film growth at $T=450^\circ$C [6, 9]) and 0.562 eV for LuPtBi (bulk growth at $T=650^\circ$C [11, 21]). These values are close to the calculated formation energies near the A points in the phase diagrams of Fig. 3(a) and (b) respectively, close to the Sb- or Bi-rich limit. Better agreement is found for the Pt vacancy in LuPtBi, which is bulk growth at higher temperature, i.e., closer to thermodynamic equilibrium.

Such hole concentrations in LuPtSb thin films and LuPtBi bulk single crystals place the Fermi level at significantly lower positions compared to the expected value in the compensated pristine materials, as shown in Fig. 4 for the case of LuPtSb. For the measured hole concentrations of $2.3 \times 10^{20}$ cm$^{-3}$ [6, 9], the Fermi level is positioned at 305-360 meV below the Fermi level in the ideal material. In order to shift the Fermi level upward by 200 meV, for example, the hole density would have to decrease to $2.8 \times 10^{19}$ cm$^{-3}$. Assuming that these holes come from Pt vacancies and each Pt vacancy contributes with 3 holes, we would have to increase the defect formation energy by 132 meV by increasing $\mu_{\text{Pt}}$ by the same amount ($\Delta \mu_{\text{Pt}} = -132$ meV). In an attempt to translate this number to the experimental control during growth (Lu/Pt/Sb fluxes in the MBE chamber), we can estimate the change in partial pressure of Pt, assuming an ideal gas. We note that this is a simplification of the experimental situation, where the fluxes in MBE are controlled by the temperature of the Knudsen cells, and relative changes are important. Yet, one can imagine that during growth the Pt atoms at the surface are in equilibrium (or close enough to equilibrium) with a flux of Pt atoms that is idealized here as an ideal gas. Keeping these approximations in mind, we estimate that a change of Fermi level by $+200$ meV would correspond to $\Delta \mu_{\text{Pt}} = -132$ meV, and that corresponds in a reduction of a factor of $\sim 8$ in the Pt partial pressure, or abundance of Pt during growth.

These results also provide an strategy for tuning the Fermi level in these materials. Since Pt vacancy is by far the lowest energy defect in most part of the allowed chemical potential region, increasing the chemical potential $\mu_{\text{Pt}}$ is a "straightforward" way of increasing the Pt vacancy formation energy, and therefore, decrease the hole density towards the pristine materials. Another way, is to use aliovalent species containing an additional electron and that replaces Pt, filling the Pt vacancies and resulting in extra electrons. This will also raise the Fermi level, eventually beyond the position in the pristine material, leading to n-type conductivity, as has been recently reported in Au-doped LuPtSb [9].

In summary, we studied the impact of native point defects on the electronic properties of the topological semimetals LuPtSb and LuPtBi using first-principles calculations. We find that Pt vacancy is by far the lowest energy defect in most of allowed chemical potential region in which these compounds are stable, and therefore, the most likely point defect to form during growth of thin films or bulk single crystals. The Pt vacancy leads to Sb dangling bond states that lie below the Fermi level, resulting in acceptor-like states and, thus, excess holes in these otherwise compensated semimetals. The calculated formation energies of the Pt vacancy are consistent with the observed hole concentrations in both LuPtSb and LuPtBi in undoped materials. Finally our results provides a guide to the experiments to refine and pinpoint individual point defects that can affect the transport and magnetoresistance properties in these topologically non-trivial half-Heusler compounds.

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