PAPER

f-Orbital based Dirac states in a two-dimensional uranium compound

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Abstract

Theoretical evidence of the existence of Dirac cones in two-dimensional UB\textsubscript{4} is provided. Dirac cones are created due to the interaction of strongly localized U anisotropic f\textsubscript{-}orbitals with the delocalized network of B p-orbitals in a bilayer honeycombed lattice. Spin–orbit coupling splits the relativistic electronic states in the vicinity of the Fermi level creating cone-shaped gaped bands. The contribution of f-orbitals to the formation of dispersive Dirac states is clearly determined with several theoretical approximations. U atom provides the exact amount of charge to stabilize the B sublattices creating a heavy-electron based material with reminiscent properties of graphene. The interplay between f- and p-orbitals of U and B atoms, respectively, is revealed as the origin of the itinerant electronic states, defying the paradox of delocalized electrons in a heavy-electron based material. Computed phonon diagram exhibits decoupled acoustic and optic modes arising from U and B atom vibrations, respectively, with frequencies of acoustic modes rather small as compared to optic modes. The dynamical properties of isoelectronic UAl\textsubscript{4} and UGa\textsubscript{4} are also analyzed.

1. Introduction

Research conducted at Los Alamos National Laboratory shows that actinide metals can be converted into less-reactive, safer storage forms, when arranged in three-dimensional arrays of linked boron clusters [1, 2]. With the metal atoms located between honeycombed layers of boron atoms, actinide borides are stable and own anti-corrosive properties [3]. Methods for the syntheses of metal borides are based on the high-temperature carbothermal/borothermal reduction of metal oxides with a boron–carbon source. Submicron metal boride powders or metal boride films have also been reported [4].

Comparatively to numerous isostructural transition metal borides, such as ZrB\textsubscript{2} [5] and MgB\textsubscript{2} [6], little is known about the electronic properties of actinide elements combined with group-III elements and, in general, studies are virtually non-existent for two-dimensional (2D) compounds based on strongly correlated f-orbitals. Progress in the synthesis of boride nanosheets with complex functionalities starts being available via chelation assisted selective extraction strategies for exfoliating layered metal borides [7]. Experimental realization of 2D actinide compounds will enable exploring the physical properties of heavy fermions in new geometric conditions, fostering the development of a theoretical framework for explaining the physics of correlated f-orbital materials in the low dimensional limit. In particular, identification of f-electrons Dirac states in 2D compounds is an unexplored, yet appealing, territory in nanosciences.

Dirac materials are characterized by high electron-mobility, low-power dissipation and a band structure where the energy of the electrons is a linear function of their speed [8–10]. These properties are found in graphene and related group IV 2D materials [11–15], and are a direct result of the hexagonal symmetry of two symmetrically equivalent sublattices. Efforts aimed at searching new materials with Dirac charge carriers led to identifying surfaces of three-dimensional topological insulators and a broad family of 2D networks of conjugated polymers [16]. Identifying a Dirac compound based on f-orbitals with dispersive electronic states similar to graphene poses a fundamental physic problem. 4f orbitals in free ions are highly localized in space due
to the shielding of outer electrons. $5f$ electrons, although spatially confined as well, are easier to remove from the atom in the lighter actinides, and become increasingly localized in energy and space for heavier actinides [17]. Transuranic elements such as Np exhibit flat, non-dispersive electronic states with high density of states in the vicinity of the Fermi energy dominated by $5f$-states, which leads to structural instabilities and favors low-symmetry phases [18]. However, combining $5f$-electrons based elements in the first part of the actinide series with some hexagonal $p$-orbital based lattices may yield delocalized states with linear dispersion close to the Fermi energy where the $f$-electrons have an important contribution.

In this paper, we provide theoretical evidence of an actinide based 2D boride material featuring delocalized $f$-orbital derived bands in the vicinity of the Fermi energy. Monolayered UB$_4$ exhibits dispersive Dirac cones with a small gap that derives from the spin–orbit coupling (SOC) of U $f$-orbitals. SOC removes Dirac point degeneracies but leaves almost intact the linear dispersion of bands at the Fermi level. First-principles calculations and a detailed analysis of the density of states of the nanostructure demonstrate that the dispersion is driven by the hybridization of the U atom $f$-orbitals with $p_z$-orbital of the B atoms, as opposed to the overlap of $f$-orbitals in the bulk. Charge balanced upon covalent bonding of the triangular network of U atoms with three types of group III atom-based hexagonal structures is at the origin of the 2D compounds stability.

2. Computational methods

Giving the correlated nature of $f$-orbitals, multiple schemes with different models of screening can be used to provide a first-principles description of the band structure of UB$_4$. The approach of choice was self-consistent density functional theory (DFT) with relativistic calculations including SOC. Even though including SOC in a DFT framework may pose some accuracy issues due to the treatment of the actinide-series $6p$ states [18, 19], band structure calculations exhibit expected results such as small band gap openings and mixing of electronic states that remove degeneracies. DFT-based calculations were performed within the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) functional for the exchange correlation, and the projector-augmented-wave method as implemented in VASP [20–22]. The electronic wave functions were computed with plane waves up to a kinetic-energy cutoff of 500 eV. The integration in the 2D $k$-space was performed using a $56 \times 56 \times 1$ Γ-centered $k$-point grid. Atomic coordinates and lattice constants were fully relaxed until the residual forces were smaller than 1 meV Å$^{-1}$. Hybrid functional based calculations were also conducted combining part of the exact Hartee–Fock exchange with semilocal approximation. Including an on-site Coulomb repulsion term on the U atom leads to artificial magnetic moments that are absent in experimental observations of paramagnetic bulk UB$_4$ [23] and, therefore, it was excluded in this study. The force-constant method and the PHONOPY package [24] were employed for computing phonon spectra and heat capacities.

3. Results and discussion

3.1. Geometry and stability

Bulk UB$_2$ is a ceramic material with a hexagonal covalent structure which may be regarded as formed by plane triangular sheets of U atoms in between flat hexagonal networks of B atoms. In monolayered UB$_4$ a triangular network of U atoms is sandwiched between two B honeycombed lattices (see figures 1(a) and (b)), so each U atom is connected by covalent bonds with twelve B atoms. The optimized lattice parameter is 3.11 Å, and the separation between parallel B layers is 3.65 Å. Nanostructures with similar geometry and based on boron and $d$-orbital transition metal atoms were studied previously [25, 26].

Charge imbalance of a stand-alone honeycombe B monolayer makes the lattices inefficient in holding structural integrity. Indeed, although the three valence electrons of a B atom can create $sp^3$ hybrid orbitals oriented in the plane at 120°, the resulting B hexagonal network is energetically not viable unless another source provides the exact amount of electrons that stabilizes the structure [27]. With each B atom accepting one electron from the valence $5f$-orbital of the U atom, the whole nanostructure becomes isoelectronic to two layers of graphene and dynamically stable, as demonstrated by the absence of negative frequencies in the phonon diagram of figure 1(c).

Considering other isoelectronic atomic elements to B such as Al and Ga atoms, the phonon diagrams of the isomorphic UA$_3$ and UGa$_4$ demonstrate the viability of both compounds as quasi-2D structures. The lattice parameters of the hexagonal cells are 4.58 Å and 4.50 Å, respectively, and the vertical separation of the B layers are 3.03 Å and 3.11 Å respectively. Although only UB$_4$ exhibits remarkable electronic features, it is worthwhile to examine the dynamical and thermal properties of the three uranium 2D compounds.

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The three layered hexagonal structures exhibit a phonon diagram with 15 phonon branches: three acoustic (LA, TA and ZA) and twelve optical modes. According to the projected density of states of figure 1(c), acoustic and optical phonon branches are dominated by atoms with larger (U) and smaller (B) mass respectively. The LA and TA modes correspond to longitudinal and transverse phonon oscillations of the U atom in the monolayer plane. Mode ZA corresponds to vibrations in the direction normal to the direction of oscillation of the former modes. LA and TA modes obey a linear dispersion law in the zone center.

As opposed to common occurrence in 2D nanostructures [28], UB4 phonon optical branches exhibit larger energy dispersion and broader distribution of phonon velocities than acoustical branches (see figure 1(c)). Due to the large difference of the atomic masses, an unusual gap between optical and acoustic modes is developed, similarly to the gap observed in bulk BAs [29–31] and Li2Te [32]. Figure 1(c) displays the phonon diagrams of the three uranium compounds with the same scale in the ordinate axis showing that this gap decreases as the mass of the atoms in the honeycombed sublattices increases. The 5.7 THz gap of 2D UB4 is reduced to 1.72 and 0.13 THz for UAl4 and UGa4, respectively. The lighter mass of B atoms allows the acoustic phonons to span a 3.7 THz range while for both the Al and Ga compounds the acoustic branches are limited to a dispersion of 2.5 THz. All three nanostructures, and specially the B-based monolayers, enable selective phonon frequency transmission, namely no kind of atomic vibration propagation is allowed in the band gap. This phonon gap (larger in UB4), the grouping of acoustic phonons (more pronounced in UGa4), and the avoid-crossing with optical branches may entail interesting phenomena in thermal transport and material’s thermal conductivity regulation, since acoustic–optical phonon backscattering is restricted by the gap [31].

Figure 2 shows the evolution of the specific heat capacity c with temperature of the three monolayered compounds. Specific heat capacity measures the ability of the materials to absorb heat, which is defined as the ratio of the supplied heat to the resulting temperature change for a unit mass of the substance. Dimensional restriction, small group velocity, confinement of the acoustic phonons, and large mass of the U atom lead to high specific heat capacities. UGa4 exhibits enhanced c at any temperature with respect to the other isomorphs, and exceeds by an order of magnitude that of graphene at low temperature. The large mass of the U atom introduces a remarkable difference with respect to other binary monolayered compounds of large atomic masses such as MoS2 and WTe2. The two dichalcogenides and graphene are also shown for comparison. At 150 K, the c of UB4 is the same as that of MoS2 and half of WTe2, whereas at room temperature the three compounds exhibit a similar c. At large temperature, the specific heat capacities of the three uranium compounds converge, as it does for the two dichalcogenides at a ~45% lower value.

In the lower temperature range, the c of U monolayers undergo two slope changes (first at ~25 K for UB4), as shown in the inset of figure 2 where the derivative of c with temperature is plotted. This noticeable change is due to the frequency gap between acoustic and optic phonon branches that can also be observed for the other two U compounds, and is absent in the lighter monolayers.

3.3. Electronic properties
The honeycombed B sublattices considered independently are energetically not viable but very efficient in accepting electrons from another source to increase their stability [27, 33]. In a simple model of interatomic charge transfer, the four f-electrons of the U atom are leading to one to each of the four B atoms, yielding two honeycombed lattices isoelectronic to graphene sandwiching a network of U cations. A covalent bond between

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**Figure 1.** Top (a), and side (b) view of a 3 × 3 two-dimensional hexagonal unit cell of UX4 for X = B, Al, Ga. (c) Phonon spectra of UB4, UAl4, and UGa4. The same y-range for the three plots accentuates the difference in the phonon dispersion, which decreases with increasing the mass of the atoms in the hexagonal lattices. The absence of negative frequencies guarantees the dynamical stability of the nanostructures.
U and B atoms with some degree of ionicity is established. The resulting 2D crystal structure belongs to the space group $P_{6}/mm$.

Although UB$_2$ and the other two uranium compounds are isostructural and isoelectronic, several fundamental differences exist in their electronic properties which depend on the difference in energy between the valence electrons of B and the Al and Ga atoms. Here we will focus on the properties of the B honeycombed lattices, whose the ability to accept the four U valence electrons yields delocalized features to the monolayered compound.

The band structure of the hexagonal 2D lattice computed in the framework of DFT within the PBE functional is plotted in figure 3. The irreducible Brillouin zone is the area delimited by the $\Gamma$, $K$, and $M$ points in the hexagonal reciprocal lattice. In the vicinity of $K$, and some meV below the Fermi level, a Dirac point is formed as a result of two bands crossing in a single point. This small electron pocket is compensated with a hole pocket formed upon two bands creating a second cone slightly above the Fermi energy level in the $M - \Gamma$ line. At the $K$ point, band crossings occur at $\sim \pm 0.3$ eV.

Due to the large size of the actinide element, the non-relativistic band structure of monolayered UB$_4$ is expected to undergo some changes when calculations are performed considering SOC. Figure 3 shows that the electron-hole remains although meV-large band gaps at each set of cones are developed. The cone lying on the $\Gamma - K$ line is distorted completely. Whereas electronic states in the valence band mix and band-crossings vanish, in the conduction band some states split. It is worth to note that the cone in the $M - \Gamma$ line remains almost intact and only a few meV-large gap is developed. Therefore, the major effect of the SOC in this energy range of the UB$_4$ spectrum is to vanish the crossing points by slightly shifting in energy the cones, and induce band crossing.

The hybrid HSE03 functional as implemented in VASP was additionally utilized to confirm the formation and shape of Dirac cones. Figure 3 shows a set of cone-shape bands touching each other at exactly the Fermi energy in the $\Gamma - K$ line while a second set meet in the $M-\Gamma$ line. As opposed to the bands observed in the PBE
calculations, no electron-hole pock is observed and the bands exhibit enhanced dispersion, more remarkable in the latter.

To elucidate the origin of each electronic band, we resort to a color scheme to represent the band structure showing the independent contribution of each atomic orbital to the electronic states. Figure 4 shows that the uranium atom 5f states have a large contribution to the Fermi energy, corroborating that U atom 5f-electrons have an itinerant character in this compound. Specifically, f−3 and f−2 orbitals have a major contribution when combined with the pz-orbitals of the B atoms.

This result points out to the combined action of charge transfer of one U f-electron to each of the four B pz-orbitals in the unit cell and the hybridization of both types of orbitals as responsible of the creation of highly dispersive states that meet in a SOC-frustrated Dirac point. The resulting structure mimics some features of graphene insofar as a closed-shell hexagonal network of atoms hosts Dirac states in the vicinity of the charge neutrality point. It must be noted that this topological features were absent in monolayered UAl4 and UGa4.

4. Conclusions

First-principles calculations have been conducted to provide theoretical evidence on the following: (i) UB4 is a charge-balanced dynamically stable 2D compound isolectronic to graphene, (ii) the itinerant character of the f-electrons of bulk UB2 is conserved in 2D UB4 which additionally hosts electronic states with a delocalized character, (iii) the heat capacity of the monolayer is larger than some of the heaviest transition-metal 2D dichalcogenides, (iv) monolayered UB4 features an infrequent acoustic-optical gap as a result of the large difference in the mass of the constituent atoms.

In addition to being promising materials for advance technology in nuclear industry, boron compounds are solid candidates to providing a platform for the study of novel properties. The results of this study contribute to creating a theoretical framework to predict and explain the physics of an actinide-based 2D material where anisotropic f-orbitals have a prominent role in the formation of delocalized states. Although the most accurate calculation scheme to characterize an f-electron material must come upon contrast with experimental observation, all levels of theory employed to obtain a description of the band structure of UB4 agree on the presence of Dirac cones in the vicinity of the Fermi level.

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Figure 4. Color-resolved band structure showing the independent contribution of each U f- and B pz-orbital. The main contribution to the Dirac cones at the Fermi level arises from the f−3- and f−2-orbitals of the U atom and the pz of the B atoms. Darker coloring represents enhanced contribution. Horizontal dashed lines point out the Fermi level.
References

[1] Smith J L and Fisk Z 1982 J. Appl. Phys. 53 7883
[2] Lupinetti A J, Fife J L, Garcia E, Dorhout P K and Abney K D 2002 Inorg. Chem. 41 2316 pMID: 11978092
[3] Su K and Sneddon L G 1993 Chem. Mater. 5 1659
[4] Rice G W and Woodin R L 1988 J. Am. Ceram. Soc. 71 C188
[5] Opeka M M, Talmy I G, Wuchina E J, Zaykoski J A and Causey S J 1999 J. Eur. Ceram. Soc. 19 2405
[6] Nagamatsu J, Nakagowa N, Muranaka T, Zenitani Y and Akimitsu J 2001 Nature 410 63
[7] James A L and Jasuja K 2017 RSC Adv. 7 1905
[8] Wehling T, Black-Schaffer A and Balatsky A 2014 Adv. Phys. 63 1
[9] Balatsky A V, Brena B, Herper H C and Sanyal B 2018 Phys. Status Solidi 12 1870334
[10] Bernevig B A, Hughes T L and Zhang S C 2006 Science 314 1757
[11] Vogt P, De Padova P, Quaresima C, Avila J, Frantzekakis E, Asensio M C, Resta A, Eallet B and Le Lay G 2012 Phys. Rev. Lett. 108 155501
[12] Grazianetti C, Cinquanta E and Molle A 2016 2D Mater. 3 012001
[13] Dvila M E, Xian L, Cahangirov S, Rubio A and Lay G L 2014 New J. Phys. 16 095002
[14] Acun A et al 2015 J. Phys.: Condens. Matter 27 443002
[15] Zhu F f, Chen W j, Xu Y, Gao C I, Guan D d, Liu C h, Qian D, Zhang S C and Jia J f 2015 Nat. Mater. 14 1020
[16] Adjizian J J, Briddon P, Humbert B, Duvall J L, Wagner P, Adda C and Ewels C 2014 Nat. Commun. 5 doi:10.1038/ncomms6842
[17] Acun A and Mattenberger K 1995 J. Alloys Compd. 223 226
[18] Söderlind P, Landa A and Sadigh B 2019 Adv. Phys. 68 1
[19] Nordström L, Wills J M, Andersson P H, Söderlind P and Eriksson O 2000 Phys. Rev. B 63 035103
[20] Kresse G and Hafner J 1993 Phys. Rev. B 48 13115
[21] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[22] Kresse G and Joubert D 1999 Phys. Rev. B 59 1758
[23] Ohkochi T, Fujimori S i, Yamagami H, Okane T, Saitoh Y, Fujimori A, Haga Y, Yamamoto E and Ōnuki Y 2008 Phys. Rev. B 78 165110
[24] Togo A and Tanaka I 2015 Scr. Mater. 108 1
[25] Lopez-Bezanilla A 2018 Phys. Rev. Mater. 2 011002
[26] Lopez-Bezanilla A 2018 2D Mater. 5 035041
[27] Tang H and Ismail-Beigi S 2007 Phys. Rev. Lett. 99 115501
[28] Molina-Sánchez A and Wirtz L 2011 Phys. Rev. B 84 155413
[29] Lindsay L, Brodido D A and Reinecke T L 2013 Phys. Rev. Lett. 111 025901
[30] Tian F et al 2018 Science 361 582
[31] Lindsay L, Brodido D A and Reinecke T L 2012 Phys. Rev. Lett. 109 095901
[32] Mukhopadhyay S, Lindsay L and Parker D S 2016 Phys. Rev. B 93 224301
[33] Tang H and Ismail-Beigi S 2009 Phys. Rev. B 80 134113