Pyridine intercalated Bi$_2$Se$_3$ heterostructures: controlling the topologically protected states

I S S de Oliveira$^1$ and R H Miwa$^2$

$^1$Departamento de Física, Universidade Federal de Lavras, C.P. 3037, 37200–000, Lavras, MG, Brazil
$^2$Instituto de Física, Universidade Federal de Uberlândia, C.P. 593, 38400–002, Uberlândia, MG, Brazil

E-mail: igor.oliveira@dif.ufu.br

Received 21 July 2015, revised 17 October 2015
Accepted for publication 2 November 2015
Published 4 December 2015

Abstract
We use ab initio simulations to investigate the incorporation of pyridine molecules (C$_3$H$_5$N) in the van der Waals (vdW) gaps of Bi$_2$Se$_3$. The intercalated pyridine molecules increase the separation distance between the Bi$_2$Se$_3$ quintuple layers (QLs), suppressing the parity inversion of the electronic states at the $\Gamma$-point. We find that (i) the intercalated region becomes a trivial insulator. By combining the pristine Bi$_2$Se$_3$ region with the one intercalated by the molecules (py-Bi$_2$Se$_3$), we have a trivial/topological heterojunction (py-Bi$_2$Se$_3$/Bi$_2$Se$_3$) characterized by the presence of topologically protected metallic states at the interfacial region. Next, (ii) we apply an external compressive pressure to the system, and the results are a decrease of the separation distance between the QLs intercalated by pyridine molecules, and the metallic states are shifted toward the bulk region, turning the system back to the insulator. Our findings indicate that, through the intercalation of pyridine molecules in Bi$_2$Se$_3$ [(i)], we may have a number of topologically protected metallic channels embedded in (py-Bi$_2$Se$_3$)$_n$/Bi$_2$Se$_3$$_{h}$ heterostructures/superlattices, in addition, through suitable tuning of the external pressure [(ii)], we can control its topological properties, turning on and off the topologically protected metallic states in (py-Bi$_2$Se$_3$)$_n$/Bi$_2$Se$_3$$_{h}$.

Keywords: topological insulator, intercalation, first-principles

(Some figures may appear in colour only in the online journal)

1. Introduction

Three-dimensional topological insulators (TIs) are insulator materials in the bulk phase, but they present metallic topological surface states (TSSs). Those TSSs are characterized by a linear energy dispersion, giving rise to an odd number of Dirac cones protected by time-reversal symmetry (TRS). The Dirac fermions present an helical spin-texture, where the spin vector lies parallel to the surface plane, and are locked perpendicularly to the surface wave vector $\mathbf{k}$. As a result, the massless Dirac fermions in TIs are protected to backscattering processes induced by time-reversal invariant impurities or defects [1–4]. However, such backscattering processes are no longer forbidden (i) in the presence of external magnetic field, e.g., due to magnetic impurities, since the TRS has been suppressed [5–9]; or (ii) due to the energy resonance between the TSSs and bulk continuous states, giving rise to scattering channels between the TSSs and the bulk states [10–12].

These materials are of great promise for spintronics applications, due to the formation of nearly dissipationless spin-polarized surface current [13]. Currently, Bi$_2$Se$_3$ (a binary chalcogenide) is one of the most investigated TI due to its large band gap (\(\sim 0.3\) eV), and nearly idealized single Dirac cone at the $\Gamma$-point [14–16]. Bi$_2$Se$_3$ presents a rhombohedral structure composed by quintuple layers (QLs) of Se and Bi atoms, forming a sequence of Se–Bi–Se–Bi–Se atoms covalently bonded; these QLs are stacked along the $c$-axis of a hexagonal structure by van der Waals (vdW) interactions.

With the aim of developing new (nano)electronic devices as well improving the understanding of the fundamental
physics of TIs, several material designs based on TIs have been proposed [17, 18]. For instance, the development of field effect transistors made of nanowires of Bi2Se3, [19] nanopolates of Bi2Se3 on graphene [20] and a few layers of Bi on Bi2Se3 and Bi2Te3 [21, 22]. The topologically protected (edge) states appear due to the formation of interfaces between a trivial insulator and a topological insulator [1]. As with Sb2Se3/Bi2Se3 trivial/topological interfaces, mediated by proximity effects [23] it is possible to make a suitable tuning of the energy and spacial positions of the topologically protected helical states [24–26]. Further control of the topological (edge) states in topological/trivial heterostructures has been performed by including TI alloys [27], as well as external electric field [28]. Moreover, recent theoretical studies have considered the effect of mechanical strain on the topological–trivial phase transition in bulk Bi2Se3 [29] and Sb2Se3 [30].

Recent experiments have explored the possibility of inserting guest species in the vdW gaps of Bi2Se3, a process known as intercalation. Koski et al [31, 32] added various zerovalent metals in the vdW gaps of Bi2Se3 nanoribbons, and it is expected that new properties and/or tuning of the Bi2Se3 properties can be achieved by intercalation, e.g., superconductivity [33]. Beside metals, molecules have been intercalated in Bi2Se3. For example, it has been shown that pyridine molecules in Bi2Se3 present interesting properties for optoelectronic applications [34].

In this work, we investigate the formation of trivial/topological heterostructures through the incorporation of pyridine molecules in the vdW gap of Bi2Se3. We verify the formation of (mechanically) switchable topologically protected metallic states embedded at the trivial/topological interface, characterized by a single Dirac cone at the Γ-point. Initially we examine the energetic stability, equilibrium geometry, and the electronic structure of Bi2Se3 intercalated by pyridine molecules (py-Bi2Se3), where we verify that the py-Bi2Se3 system is a trivial insulator. By considering a hetero-junction composed of py-Bi2Se3 and pristine Bi2Se3 (py-Bi2Se3/Bi2Se3), we analyze (i) the occurrence of topologically protected metallic states in py-Bi2Se3/Bi2Se3, and (ii) the control of those metallic states (turning on and off) upon the application of external pressure.

2. Computational details

The calculations are performed based on the density-functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) [35]. We use the generalized gradient approximation (GGA), in the form proposed by Perdew, Burke, and Ernzerhof [36], to describe the exchange-correlation functional. The Kohn-Sham orbitals are expanded in a plane-wave basis set with an energy cutoff of 400 eV. The electron–ion interactions are taken into account using the Projector Augmented Wave (PAW) method [37]. All geometries were relaxed until the atomic forces were lower than 0.02 eV/Å. The Brillouin Zone is sampled according to the Monkhorst-Pack method [38], using at least a $3 \times 3 \times 1$ mesh. We also used a functional that accounts for dispersion effects, representing van der Waals (vdW) forces, according to the method developed by Tkatchenko-Scheffler (TS) [39], which is implemented on VASP [40]. The inclusion of van der Waals forces in the simulations is necessary to obtain the correct vdW gap between two QLS [41]; the interaction between molecule and Bi2Se3 is also better described with the inclusion of vdW interactions.

3. Results and discussion

Initially we calculate the equilibrium distance ($z_0$) between two consecutive QLS of Bi2Se3, vdW gap. Here we have considered two isolated QLS and minimize the total energy as a function of the width of vdW gap ($\Delta z$). As shown in figure 1 (squares), we find the energy minimum for $z_0 = 2.65$ Å; this result is in agreement with experimental measurements [42], and recent theoretical studies [41, 43]. By using the same procedure, we determine $z_0$ upon the presence of a pyridine molecule intercalated in between the QLS. The QLS present a $2 \times 2$ surface periodicity, which corresponds to a molecular concentration of $1.64 \times 10^{-2}$ molecules/Å$^2$. In this case, we find that (i) there is no chemical bonding between the molecule and the Bi2Se3 QLS, and (ii) the vdW gap increases by 3.85 Å, $z_0 = 2.65 \rightarrow 6.50$ Å, figure 1 (circles). Such an increase of the vdW gap reduces the binding energy between the QLS, however, the formation of pyridine intercalated Bi2Se3 QLS is still an exothermic process.

To determine whether the material behaves as a trivial or topological insulator, we analyze the parity change between valence and conduction bands mediated by spin–orbit coupling (SOC) [44]. In Bi2Se3 the SOC induces a band inversion between Se-pz (Bi-pz) orbitals near the valence (conduction) band maximum (minimum) at the Γ-point. Such a band inversion does not occur in the other time-reversal invariant points of the Brillouin zone [14, 29]. The same procedure was applied to examine if such a band inversion still occurs in pyridine intercalated Bi2Se3 QLS and the intercalated molecules were fully relaxed.

Figure 1. Formation energy for two Bi2Se3 QLs at various separation distances, as represented in the structure shown on the right. The black line (squares) represents the pristine system and the red line (circles) the system with a pyridine molecule intercalated between the two QLS.
intercalated Bi$_2$Se$_3$ system. Our results are presented in Figure 2. Band structures for (a) Bi$_2$Se$_3$ bulk with intercalated pyridine molecules excluding SOC; and in (b) including SOC. (c) Bi$_2$Se$_3$ bulk with the vdW gap obtained in the system with intercalated molecules (figure 1), excluding SOC, and in (d) including SOC. The symbols are contributions of pz-orbitals for Se (red) and Bi (green) atoms.

Bi$_2$Se$_3$. By considering the pyridine concentration of 1.64 × 10$^{-2}$ molecules/Å$^2$ intercalated in Bi$_2$Se$_3$, we verify that when the SOC is not included the py-Bi$_2$Se$_3$ system is an insulator, where the valence band maximum is dominated by Se-pz orbitals and the conduction band minimum by Bi-pz orbitals (figure 2(a)), as observed for the pristine Bi$_2$Se$_3$ bulk. In contrast, by turning SOC on we observe the lack of band inversion around the Γ-point (figure 2(b)), which suggests that pyridine molecules intercalated in Bi$_2$Se$_3$ bulk suppress their topological properties, i.e., the py-Bi$_2$Se$_3$ system is a trivial insulator.

This topological–trivial transition in the Bi$_2$Se$_3$ structure is possibly caused by the increase in the vdW gaps due to the pyridine intercalation [45, 46]. In order to verify such an assumption, we calculate the electronic band structure of Bi$_2$Se$_3$, but keeping the equilibrium geometry of the pyridine intercalated Bi$_2$Se$_3$ system. Our results are presented in figures 2(c) and (d). By turning off and on the SOC we observe that the band inversion at the Γ-point is still absent. Furthermore, due to the large distance between the QLs ($z_0 = 6.50$ Å), and the absence of chemical bonding between the molecule and the Bi$_2$Se$_3$ QLs, each QL of py-Bi$_2$Se$_3$ somewhat mimics a free-standing monolayer film of Bi$_2$Se$_3$, which is a trivial insulator [47, 48].

In experiments we would most likely observe regions with pyridine molecules intercalated between the vdW gaps and regions of pristine Bi$_2$Se$_3$, and as a result we may have a trivial/topological insulator heterojunction composed by py-Bi$_2$Se$_3$ and Bi$_2$Se$_3$ (py-Bi$_2$Se$_3$/Bi$_2$Se$_3$). To simulate such a heterojunction, we considered a supercell containing nine QLs, where we have three QLs intercalated by the molecules and six consecutive pristine QLs (py-Bi$_2$Se$_3$)$_3$/(Bi$_2$Se$_3$)$_6$. As shown in figure 3, the pyridine molecules are intercalated between QL(1) and QL(4), characterizing the (py-Bi$_2$Se$_3$)$_3$ region, and QL(4)/QL(5)/.../QL(9)/QL(1) forms the pristine (Bi$_2$Se$_3$)$_6$ region. Given that geometry, the trivial/topological interface are characterized by QL(1) and QL(4). Band structure calculations reveal the presence of metallic states forming a Dirac-like cone at the Γ-point, indicated by the solid lines in figure 3. To localize these states we compute the pz-orbitals contribution from various QLs around the Γ-point, and project these states in the energy levels shown in the band structure [49]. We find that the electronic states around the Dirac point are mainly attributed to the Bi pz-orbitals lying at the py-Bi$_2$Se$_3$/Bi$_2$Se$_3$ interface region, QL(1) and QL(4). In contrast, there are no electronic contribution to the metallic states from the py-Bi$_2$Se$_3$ bulk region, QL(2) and QL(3). Somewhat similarly, the electronic contributions to the Dirac-like cone coming from the bulk region of Bi$_2$Se$_3$ [QL(5)–QL(8)] are almost negligible. These findings allow us to conclude that (py-Bi$_2$Se$_3$)$_m$/(Bi$_2$Se$_3$)$_n$ heterostructures (or superlattices) create topologically protected metallic states, embedded at the trivial/topological interface region. However, it is worth noting that the appearance of those topologically protected surfaces states depends on the thickness ($n$) of the (Bi$_2$Se$_3$)$_n$ film [47, 48]. Indeed, theoretical studies performed by Yazyev et al [50] indicate that at least three QLS ($n = 3$) are necessary for the formation of topologically protected surface states in Bi$_2$Se$_3$. Moreover further theoretical studies [46] found the formation of TSSs for an interlayer spacing (vdW gap) larger than ∼5.5 Å in Bi$_2$Se$_3$. Thus, we
can infer that it is possible to get topologically protected metallic channels by considering few layers of py-Bi\(_2\)Se\(_3\) embedded in Bi\(_2\)Se\(_3\).

In order to verify the statement above, we construct a supercell containing one molecule separated by six Bi\(_2\)Se\(_6\) QLs, (py-Bi\(_2\)Se\(_3\))\(_n_1\)/(Bi\(_2\)Se\(_6\))\(_n_3\), which is shown in figure 4(c). Indeed, we find the TSSs forming a Dirac-like cone at the \(\Gamma\)-point, as shown in figure 4(a). Those states lie at the (py-Bi\(_2\)Se\(_3\))\(_n_1\)/(Bi\(_2\)Se\(_6\))\(_n_3\) interface region. The spin texture of TSSs is constrained by the time reversal symmetry. Here we calculate the expected value of spin-polarization components \(\langle S_n(k)\rangle\) for the TSSs, of (py-Bi\(_2\)Se\(_3\))\(_n_1\)/(Bi\(_2\)Se\(_6\))\(_n_3\) near the \(\Gamma\)-M and \(\Gamma\)-K directions. As depicted in the inset of figure 4(a), for the electronic states parallel to the \(\Gamma\)-M direction, we find (i) positive (negative) values of \(\langle S_{n,x}(k)\rangle\) for the occupied (empty) states, while (ii) \(\langle S_{n,z}(k)\rangle = \langle S_{n,y}(k)\rangle = 0\); whereas for \(k\) parallel to the \(\Gamma\)-K direction, we find (iii) negative (positive) values of \(\langle S_{n,y}(k)\rangle\) for the occupied (empty) states, (iv) \(\langle S_{n,z}(k)\rangle = 0\), and (v) \(\langle S_{n,z}(k)\rangle\) values are negligible around the \(\Gamma\)-point. Such a picture of \(\langle S_{n,z}(k)\rangle\), for the TSSs lying at the (py-Bi\(_2\)Se\(_3\))\(_n_1\)/(Bi\(_2\)Se\(_6\))\(_n_3\) interface, is practically the same as that obtained for the TSSs on the Bi\(_2\)Se\(_3\)(111) surface [8, 50].

We have to take into account that there are two (adjacent) Bi\(_2\)Se\(_3\) surfaces in (py-Bi\(_2\)Se\(_3\))\(_n_1\)/(Bi\(_2\)Se\(_6\))\(_n_3\), separated by a layer of pyridine molecules, where each surface presents TSSs with opposite spin-helicity. In this case, although those surfaces are separated by an vertical distance \(z_0\) of 6.50 Å, we may have backscattering processes upon electron tunneling between those surfaces. Such an electron tunneling, and thus backscattering rate, can be (controlled) reduced by adding pyridine layers in the vdW gaps of Bi\(_2\)Se\(_3\). For instance, in (py-Bi\(_2\)Se\(_3\))\(_n_2_1\)/(Bi\(_2\)Se\(_6\))\(_n_3\), the adjacent surfaces, with TSSs with opposite spin-helicity, are separated by about 20 Å.

We now propose a mechanism to gain control over the topologically protected metallic states in (py-Bi\(_2\)Se\(_3\))\(_n_1\)/(Bi\(_2\)Se\(_6\))\(_n_3\). Decreasing the separation distance between the QLs separated by the molecules we expect the suppression of the TSSs, as the vdW gap approaches its bulk value. We then consider the (py-Bi\(_2\)Se\(_3\))\(_n_1\)/(Bi\(_2\)Se\(_6\))\(_n_3\) system and apply a compressive pressure directed along the \(c\)-axis, namely normal to the QLs, decreasing the separation distance in the vdW gap \(\Delta z\) from 6.50 to 4.12 Å, upon an external pressure of \(P \approx 9.1\) GPa. This (pressure) value is comparable to the ones achieved experimentally for Bi\(_2\)Se\(_3\) structures [51, 52]. The energy difference between the relaxed and compressed (py-Bi\(_2\)Se\(_3\))\(_n_1\)/(Bi\(_2\)Se\(_6\))\(_n_3\) is shown in the upper part of figure 5. An energy of \(\sim 10\) meV/Å\(^2\) needs to be added to compress the system from \(\Delta z = 6.50\) to 4.12 Å. In the lower part of figure 5 we show the band structure for four values of \(\Delta z\), starting from 6.50 Å, which has already been shown to have metallic states. For \(\Delta z = 5.65\) Å, the metallic states at the \(\Gamma\)-point are still present. Upon further decrease of \(\Delta z\), the metallic states start to move in the bulk band direction. For \(\Delta z = 4.71\) Å, the Dirac point has been suppressed, as we find an energy gap at the \(\Gamma\)-point. The energy gap at the \(\Gamma\)-point is even larger for \(\Delta z = 4.12\) Å, washing out the TSSs at the (py-Bi\(_2\)Se\(_3\))\(_n_2_1\)/(Bi\(_2\)Se\(_6\))\(_n_3\) interface region. By removing the pressure the system can reversibly return to its original geometry, and again the metallic states will be present. Thus, we can combine pressure application and pyridine molecules intercalation to the Bi\(_2\)Se\(_3\) structure to turn the topologically protected metallic states on and off, going from an insulator to a semi-metallic material by taking advantage of the TI properties of Bi\(_2\)Se\(_3\). The results presented above can be
extended to any number of QLs intercalated by molecules, assuring that we have a Bi$_2$Se$_3$/py-Bi$_2$Se$_3$ junction [4].

4. Conclusions

We have performed an ab initio study of pyridine molecules intercalated in the vdW gaps of Bi$_2$Se$_3$ (py-Bi$_2$Se$_3$). In py-Bi$_2$Se$_3$ the inter-QL distance increases, which turns the TI material into a trivial insulator. (i) By considering py-Bi$_2$Se$_3$/Bi$_2$Se$_3$ heterojunctions, we find a trivial/topological interface, characterized by the presence of topologically protected metallic states (forming a Dirac-like cone) embedded at the interface region of the heterostructure. Those metallic states are protected from the (external) environment, since they are embedded in (py-Bi$_2$Se$_3$)$_m$/Bi$_2$Se$_3$)$_n$. Such metallic states can be present even for a single QL incorporated by pyridine molecules (py-Bi$_2$Se$_3$)$_3$/Bi$_2$Se$_3$)$_n$. Lastly, (ii) we have shown the possibility to control the occurrence of such metallic states in (py-Bi$_2$Se$_3$)$_m$/Bi$_2$Se$_3$)$_n$, upon an external compressive strain; turning-on and -off those metallic states at the heterojunction interface. Therefore, our results suggest that through a suitable intercalation of organic molecules in the vdW gap of layered topological insulators, it is possible to design trivial/topological superlattices, like the (py-Bi$_2$Se$_3$)$_m$/Bi$_2$Se$_3$)$_n$ examined in the present study, characterized by a (large and controllable) number of topologically protected metallic channels switchable by an external compressive strain.

Acknowledgments

This work was supported by the Brazilian Nanocarbon Institute of Science and Technology (INCT/Nanocarbono), and the Brazilian agencies CNPq and FAPEMIG. The authors also acknowledge the computational support from CENAPAD/SP.

References

[1] Hasan M Z and Kane C L 2010 Rev. Mod. Phys. 82 3045–67
[2] Zhang T et al 2009 Phys. Rev. Lett. 103 266803
[3] Roushan P, Seo J, Parker C V, Hor Y S, Hsieh D, Qian D, Richardella A, Hasan M Z, Cava R J and Yazdani A 2009 Nature 460 1106
[4] Seo J, Beidenkopf P R H, Hor Y S, Cava R J and Yazdani A 2010 Nature 466 343
[5] Wray L A, Xu S, Xia Y, Hsieh D, Fedorov A V, Hor Y S, Cava R J, Bansil A, Lin H and Hasan M Z 2011 Nat. Phys. 7 32
[6] Chen Y L et al 2010 Science 329 659
[7] Xu S Y et al 2012 Nat. Phys. 8 616
[8] Abdalla L B, Seixas L, Schmidt T M, Miwa R H and Fazzio A 2013 Phys. Rev. B 88 045312
[9] Schmidt T M, Miwa R H and Fazzio A 2011 Phys. Rev. B 84 245418
[10] Analytis J G, Chun J-H, Chen Y, Corredor F, McDonald R D, Shen Z X and Fisher I R 2010 Phys. Rev. B 81 205407
[11] Butch N P, Kirshenbaum K, Syers P, Sushkov A B, Jenkins G S, Drew H D and Paglione J 2010 Phys. Rev. B 81 241301(R)
[12] Kim S et al 2011 Phys. Rev. Lett. 107 056803
[13] Pesin D and MacDonald H 2012 Nat. Mater. 11 409
[14] Zhang H, Liu C X, Qi X L, Dai X, Fang Z and Zhang S C 2009 Nat. Phys. 5 438
[15] Xia Y et al 2009 Nat. Phys. 5 398
[16] Hsieh D et al 2009 Nat. Lett. 460 1101
[17] Kong D and Cui Y 2011 Nat. Chem. 3 845
[18] Cha J J, Koski K J and Cui Y 2013 Phys. Status Solidi 7 15
[19] Zhu H et al 2013 Sci. Rep. 3 1757
[20] Dang W, Peng H, Li H, Wang P and Liu Z 2010 Nano Lett. 10 2870
[21] Miao L et al 2013 PNAS 110 2758
[22] Wang Z, Yao M-Y, Ming W, Miao L, Zhu F, Liu C, Gao C, Jia D Q J-F and Liu F 2013 Nat. Commun. 4 1384
[23] Hutason J A and Stanescu T D 2011 Phys. Rev. B 84 085103
[24] Wu G, Chen H, Sun Y, Li X, Cui P, Franchini C, Wang J, Chen X-Q and Zhang Z 2013 Sci. Rep. 3 1233
[25] Seixas L, West D, Fazzio A and Zhang S 2015 Nat. Commun. 6 7630
[26] Menshov V N, Tugushev V V, Ereemeev S V, Echenique P M and Chulkov E V 2015 Phys. Rev. B 91 075307
[27] Yoshihimi R, Tsukazaki A, Kikutake K, Cheekelsky J G, Takahashi K S, Kawasaki M and Tokura Y 2014 Nat. Mater. 13 253
[28] Menschikova T V, Otrokov M M, Tsirkin S S, Samorokov D A, Bebneva V V, Ernst A, Kuznetsov V M and Chulkov E V 2013 Nano Lett. 13 6064
[29] Young S M, Chowdhury S, Walter E J, Mele E J, Kane C L and Rappe A 2011 Phys. Rev. B 84 085106
[30] Li W, Wei X-Y, Zhu J-X, Ting C S and Chen Y 2014 Phys. Rev. B 89 035101
[31] Koski K J, Wessells C D, Reed B W, Cha J J, Kong D and Cui Y 2012 J. Am. Chem. Soc. 134 13773–9
[32] Koski K J, Cha J J, Reed B W, Wessells C D, Kong D and Cui Y 2012 J. Am. Chem. Soc. 134 7584–7
[33] Hor Y S, Williams A J, Cheekelsky J G, Roushan P, Seo J, Xu Q, Zandbergen H W, Yazdani A, Ong N P and Cava R J 2010 Phys. Rev. Lett. 104 057001
[34] Cha J J, Koski K J, Huang K C Y, Wang K X, Luo W, Kong D, Yu Z, Fan S, Brongersma M L and Cui Y 2013 Nano Lett. 13 5913–8
[35] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[36] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[37] Kresse G and Joubert D 1999 Phys. Rev. B 59 1758
[38] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188
[39] Tkatchenko A and Scheffler M 2009 Phys. Rev. Lett. 102 070305
[40] Bucko T, Lèbègue S, Hafner J and Angyán A 2013 Phys. Rev. B 87 064110
[41] Lind H, Lidin S and Häussermann U 2005 Phys. Rev. B 72 241305
[42] Lind H and Lidin S 2003 Solid State Sci. 5 47–57
[43] Zhang W, Yu R, Zhang H J and Fang Z 2010 New J. Phys. 12 065013
[44] Fu L and Kane C L 2007 Phys. Rev. B 76 045302
[45] Eremeev S V, Vergniory M G, Menshchikova T V, Shaposhnikov A A and Chulkov E V 2012 New J. Phys. 14 113030

[46] Seixas L, Abdalla L B, Schmidt T M, Fazzio A and Miwa R H 2013 J. Appl. Phys. 113 023705

[47] Zhang Y et al 2010 Nat. Phys. 6 584

[48] Sakamoto Y, Hirahara T, Miyazaki H, Kimura S and Hasegawa S 2010 Phys. Rev. B 81 165432

[49] Park K, Heremans J J, Scarola V W and Minic D 2010 Phys. Rev. Lett. 105 186801

[50] Yazyev O V, Moore J E and Louie S G 2010 Phys. Rev. Lett. 105 266806

[51] Hanlin J J, Jeffries J R, Butch N P, Syers P, Zocco D A, Weir S T, Vohra Y K, Paglione J and Maple M B 2012 J. Phys.: Condens. Matter 24 035602

[52] Kirshenbaum K et al 2013 Phys. Rev. Lett. 111 087001