Topological transitions to Weyl states in bulk Bi$_2$Se$_3$: Effect of hydrostatic pressure and doping

Sudip Kumar Saha,$^1$ Hrisht Banerjee,$^2$ and Manoranjan Kumar$^1$

$^1$Department of Condensed Matter Physics & Materials Sciences, S.N. Bose National Centre for Basic Sciences, JD Block, Sector-III, Salt Lake City, Kolkata 700 098, India

$^2$Institute of Theoretical and Computational Physics, Graz University of Technology, NAWI Graz, Petersgasse 16, Graz, 8010, Austria

(Dated: November 17, 2020)

Bi$_2$Se$_3$, a layered three dimensional (3D) material, exhibits topological insulating properties due to presence of surface states and a band gap of 0.3 eV in the bulk. We study the effect hydrostatic pressure $P$ and doping with rare earth elements on the topological aspect of this material in bulk from a first principles perspective. Our study shows that under a moderate pressure of $P>7.9$ GPa, the bulk electronic properties show a transition from an insulating to a Weyl semi-metal state due to band inversion. This transition may be correlated to a structural transition from a layered material to a 3D system observed at $P=7.9$ GPa. At large $P$ density of states have significant value at the Fermi-energy. Intercalating Gd with a small doping fraction between Bi$_2$Se$_3$ layers drives the system to a metallic anti-ferromagnetic state, with Weyl nodes below the Fermi-energy. At the Weyl nodes time reversal symmetry is broken due to finite local field induced by large magnetic moments on Gd atoms. However, substituting Bi with Gd induces anti-ferromagnetic order with an increased direct band gap. Our studies provides novel approaches to tune topological transitions, particularly in capturing the elusive Weyl semimetal states, in 3D topological materials.

I. INTRODUCTION

Topological insulators (TI) have potential future application in quantum computers and spintronics owing to existence of symmetry protected edge or surface states, and also provide a fundamental bridge between high-energy and condensed-matter physics due to the presence of exotic physical states in the system. These materials exhibit insulating bulk and metallic surface states and these properties lead to extensive theoretical and experimental studies. These systems show non-trivial topological order by conserving the particle number and time reversal symmetry.

The primary feature of the TI state is the inverted band structure, which results from the crossing of the valence and conduction bands of different parity symmetry, and Bi$_2$Sb$_{1-x}$ family of materials are a prime example of three dimensional (3D) materials with $Z_2$ invariant symmetry. Bi$_2$Te$_3$, Bi$_2$Te$_3$ and Bi$_2$Se$_3$ are 3D material topological layered materials. Bi$_2$Se$_3$ forms effectively two dimensional (2D) layered structures and theoretical studies predict that Bi$_2$Se$_3$ has a topologically non-trivial bulk energy gap of 0.3 eV. The topological surface states are described by a single gapless Dirac cone at the Γ point. It is interesting to understand the mechanism which may close bulk energy gap in Bi$_2$Se$_3$.

Bi$_2$Se$_3$ and its family of materials have been extensively explored, by applying pressure, doping Bi with rare earth (RE) atoms like Gd, Sm etc. and also with transition metal (TM) atoms like Cr, Fe, etc. Incorporating impurities with large magnetic moment may break time reversal symmetry and lead to many exotic phenomena one of which is quantum anomalous hall effect (QAHE). The QAHE in material supports dissipationless charge transport which is very highly desirable experimentally. Mn-doped Bi$_2$Se$_3$ shows spin glass like behaviour, and Fe-doped Bi$_2$Se$_3$ exhibits dominance of ferromagnetic interactions, whereas Cr-doped Bi$_2$Se$_3$ favors ferromagnetic interactions. However, small (less than 0.1 %) doping of Cr doped materials are reported as ferromagnetic, while Fe-doped Bi$_2$Se$_3$ tends to be weakly anti-ferromagnetic. Cr and Fe-doped Bi$_2$Se$_3$ are insulating, but the band gaps are substantially reduced due to the strong hybridization between the $d$ orbital of the dopants and the $p$ orbitals of the neighboring Se atoms. There are some reports of intercalating and doping topological materials which exhibit exotic behaviour like Bi$_2$Se$_3$ doped with Cu at doping fractions of 0.12 and 0.15 show intermixing of both Cu-intercalation between Se-Se layers and Cu-substitution in Bi-layer sites. Superconducting transitions in Cu-intercalated Bi$_2$Se$_3$ is observed experimentally with $T_C$ of 3.5 K and 3.6 K for doping fraction 0.12 and 0.15 respectively. Metallic behavior in the Bi$_2$Se$_3$ crystals and paramagnetic features are observed in the low temperature region of the Cu-doped samples. Intercalating of Cu in this material also holds the promise of topological superconductivity.

Rare earth (RE) atoms with 4$f$ electrons are expected to be better candidates to introduce FM order in TIs compared to 3$d$ TM. Ionic radii of RE atoms are larger than TM atoms and RE elements match Bi$_2$Se$_3$ lattice better than TM. Hence a smaller structural distortion is expected due to small lattice mismatch, and no disorder is observed. RE atoms are better dopants in avoiding impurity aggregation which is seen in Cr (TM) doped (Bi,Sb)$_2$Te$_3$ which is responsible for mag-
A pressure induced transition to a topological phase has to a high pressure body-centered tetragonal phase (SG: bient rhombohedral phase (Space group (SG): R̅3m) to a progressive structural evolution occurs from an am-

ond anvil cell (DAC) at a pressure of 11GPa on application of pressure via dia-

pressure of very high pressures phase transitions have been experimentally observed at (CB) intersects at two points at

t preserves the time-reversal and inversion symme-

ty. If band dispersion near the crossing point is lin-

CREASE the hybridization between the orbitals, and a re-

of this phenomena exists till date.

application of pressure is an important tool to en-

hance the hybridization between the orbitals, and a re-

cent study shows the emergence of an unconventional

superconducting phase in topological Bi$_2$Se$_3$ at a critical

pressure of 11GPa on application of pressure via dia-

mond anvil cell (DAC)

Pressure induced structural phase transitions have been experimentally observed at very high pressure

The experiments indicate that a progressive structural evolution occurs from an ambient rhombohedral phase (Space group (SG): R3m) to monoclinic phase (SG: C2/m) at 36GPa and eventually to a high pressure body-centered tetragonal phase (SG: H4/mmm) at 81GPa on application of pressure via DAC. A pressure induced transition to a topological phase has been found in Bi$_2$S$_3$ at a pressure of 5.3GPa exerted via DAC

In some of topological materials like TaAs single crystals the valance band (VB) and the conduction band (CB) intersects at two points at ± k near the Fermi energy. If band dispersion near the crossing point is linear due to relativistic nature of fermions and the system preserves the time-reversal and inversion symme-

try, then the system may be characterised as a Weyl semimetal (WSM). In WSMs non-orthogonal magnetic and electric fields results in a novel observation of chiral anomaly. This results in the chiral-magnetic effect which is the observation of an unconventional negative longitudinal magnetoresistance

In this article we investigate the effect of hydrostatic pressure (HP), and doping with a rare earth element on bulk phase of Bi$_2$Se$_3$, a probable 3D TI, from the perspec-
tive of ab-initio density functional theory (DFT) based calculations. The material shows a transition from a small bulk band gap insulator at low HP, to a gapless dirac state at a critical pressure 7.9 GPa, and to a WSM beyond the critical pressure. To the best of our knowl-

eedge this is the first prediction of a WSM state arising due to the application of pressure in Bi$_2$Se$_3$ family of materials. We also note that Bi$_2$Se$_3$ undergoes a transition from a layered material to 3D topological material on applying 7.9 GPa HP.

We also study the effect of intercalation of Gd atoms between the Bi$_2$Se$_3$ quintuple layers (QL) as well as partially substituting Bi with Gd in bulk Bi$_2$Se$_3$. While intercalating Gd between the QLs shows a broad band-width metallic ground state, with a time reversal symmetry broken Weyl like feature in the band structure below the Fermi energy; substituting Bi with Gd shows an increase in band gap and an insulating state. This results from differential bonding introduced due to the differ-

ent ways of doping the material. Thus we propose that a tunable topological transition to Weyl states may be driven in 3D bulk Bi$_2$Se$_3$ by the effect of both application of hydrostatic pressure and intercalating with rare earth elements, to attain the exciting and elusive Weyl like states. Our study is expected to open up further experimental investigations in the tunability of topologi-

cal transitions in bulk phases of 3D topological materials particularly in context of experimental realisation of such Weyl semimetal states.

The paper is divided into five sections, we describe the computational method in section II. The results are di-

vided into two major sections. In section III we describe the effect of pressure on structural and electronic prop-

erties. The effect of doping is studied in section IV. The summary and comparison of results are given in section V.

II. COMPUTATIONAL DETAILS

Our first-principles calculations were carried out in the plane wave basis as implemented in the Vienna Ab-initio Simulation Package (VASP) with projector-augmented wave (PAW) potential. The exchange-correlation func-

tional used in the calculations is the generalized gra-

dient approximation (GGA) implemented following the Perdew-Burke-Ernzerho prescription. Local correla-

tions are taken into account wherever necessary with the energy correction within the framework of GGA+U formalism primarily for dopant Gd atoms, with values of $U = 6eV, J = 1eV$. For ionic relaxations, internal pos-

itions of the atoms are allowed to relax until the forces
became less than 0.005 eV/Å\(^2\). Energy cutoff used for calculations is 500 eV, and \(6 \times 6 \times 4\) Monkhorst-Pack k-points mesh provide a good convergence of the total energy in self-consistent field calculations. The spin-orbit coupling (SOC) in Bi atoms is treated as a perturbative non-self consistent correction which is better suited for topological materials\(^{[53]}\). In order to study the effect of hydrostatic pressure, calculations are done by first changing the volume of the unit cell isotropically and then relaxing the ionic positions for each of the modified volume.

### III. EFFECT OF HYDROSTATIC PRESSURE \(P\)

In this section we discuss the effects of the application of hydrostatic pressure (HP) \(P\) on bulk band structure of Bi\(_2\)Se\(_3\). The HP induced structural transition, and changes in lattice parameters are analysed in first subsection, and a systematic study of the effect of structural transition on the band structure properties of Bi\(_2\)Se\(_3\) are provided in the next subsection. Generally, pressure pushes the atoms closer to each other, and leads to enhancement in effective hybridization of orbitals which result in reduction of band gap. In large \(P\) limit structural transition is also a possibility. In this section we study the structural behaviour of Bi\(_2\)Se\(_3\) first, and then analyse the effect of pressure induced structural transitions on the electronic properties.

#### A. Change in crystal structure

We first discuss the basic structural details of the material at \(P = 0\) GPa, and thereafter, the structural changes are analysed at various pressures. Bi\(_2\)Se\(_3\) has a hexagonal symmetry with space group R\(\overline{3}\)m, and with lattice parameters \(a=b=4.142\) Å, \(c=28.637\) Å and lattice angles \(\alpha = \beta = 90^\circ\), \(\gamma = 120^\circ\). Bi\(_2\)Se\(_3\) forms quintuple layers (QL) within the hexagonal unit cell as seen from Fig. 1a. The crystal structure along the \(c\)-axis direction consists of QLs of two Bi layers sandwiched between three Se layers, Se\(_2\)-Bi-Se\(_2\)-Bi-Se\(_1\), where the subscript indicates that the two Se atoms are in-equivalent by symmetry (cf Fig. 1). The atoms within each QL are chemically bonded, but the QLs are weakly bonded through van der Waals interaction. Bi\(_2\)Se\(_3\) slabs consist of an integer number of QLs.

To understand the structural phase transition with pressure \(P\), \(c/a\) ratio and distance between Se-Se atoms sitting at two nearest QL \(d_{Se-Se}\) are studied, and we note that \(c/a\) ratio decreases with \(P\) up to \(P = P_c = 7.9\) GPa, and then it increases on increment of \(P\) as shown in Fig. 2a. Variation of lattice parameter \(a\), \(b\) and \(c\) and \(c/a\) with \(P\) are provided in Table I in the Appendix. The distance between the two Se atoms from two nearest QL \(d_{Se-Se}\) continuously decreases with \(P\), and at \(P = P_c\) GPa the Se-Se distance decreases to below 2.17 Å which is less than bond length of diatomic Se\(_2\), therefore at \(P_c\) GPa a structural phase transition occurs as shown in Fig. 2b. For \(P > P_c\) Bi\(_2\)Se\(_3\) behaves like three dimensional (3D) structure rather a layered structure, as demonstrated in Fig. 2c, which is also confirmed from the charge density which are not shown here for the sake of brevity.

The bond distances from Bi to Se\(_1\), \(d_{Bi-Se1}\), and to Se\(_2\), \(d_{Bi-Se2}\), decrease on application of pressure. The bond angles \(\angle Se1-Bi-Se1\) and \(\angle Se2-Bi-Se2\) also decrease with increase of \(P\), however due to bending of the bonds, \(\angle Se1-Bi-Se2\) increases with increase of \(P\) as shown in Table II in the appendix.

#### B. Change in electronic structure

We study the change in electronic structure of Bi\(_2\)Se\(_3\) with application of hydrostatic pressure as shown in Fig. 3. The band structure at zero applied pressure has a band gap of 0.3 eV at the \(\Gamma\) point and both Bi and Se have partially filled \(p\)-orbitals which participate to form energy bands as seen from the projected DOS in Fig. 5. The valence bands are primarily Se-\(p\) bands, whereas, the conduction bands are Bi-\(p\) bands as shown in Fig. 3. Based on symmetry analysis we find that the \(p\) levels on the Bi and Se\(_1\) are split by the crystal symmetry into \(p_z\) and \(\left( p_x, p_y \right)\) at the \(\Gamma\) point. The band gap is formed...
between the bonding and anti-bonding states resulting from the hybridization of $p_x$ orbitals on the Bi and Se sites. Considering surface calculations the band structure of Bi$_2$Se$_3$ shows the presence of surface states at the $\Gamma$ point which is a typical signature of topological insulators at $P = 0$ (not shown here).

We apply HP $P$ systematically on the system and notice that the band gap decrease with $P$ and it is 0.05 eV and 0.009eV at $P = 5.5$ and 7.3 GPa respectively. The band gap vanishes completely at $P = 7.3$ GPa marks the point of structural transition from a layered 2D structure to a 3D structure. The bottom panel (b) and (c) shows the structures at two different pressures before and after the critical pressure for structural phase transition.

In a Weyl semimetal other than CB and VB coinciding within some energy window, the degeneracy is expected to be robust to small parametric perturbation. The double degeneracy may arise in presence of time reversal T and inversion symmetry P or their combined PT presence in the system i.e. for inversion symmetry $E_{n\sigma}(k) = E_{n\sigma}(-k)$, for time reversal symmetry $E_{n\uparrow}(k) = E_{n\downarrow}(k)$ and in combined PT symmetry $E_{n\uparrow}(k) = E_{n\downarrow}(-k)$ conditions are satisfied. These conditions are easily fulfilled in case of band inversion, i.e., the two branches of a band undergo an accidental band crossing and give rise to Weyl points, and this is applicable in our case. However the degeneracy of crossing point are preserved only in case special symmetry in the lattice, and the symmetry prevents the repulsion of degenerate points to keep the four fold degeneracy intact. Bi$_2$Se$_3$ has R3m crystal symmetry and under pressure the distance between the QLs reduces and gives rise to three dimensional structure. For $P > 7.3$ GPa, the Bi-$p$ band and Se-$p$ band crosses at $K_x = \pm 0.045$ and $E_f = 0$ at $P = 24.6$ GPa as shown in Fig. 4 a. The crossing point shown in the Fig. 4 is along the $\Gamma$-C line, but similar crossing can be found along other $\Gamma$-K momentum axis.

In absence of any external perturbation, the band dispersion near the Weyl point varies as $E(k) = \sqrt{m^2 + v^2k^2}$ with momentum $k$ where $m$ and $v$ are mass and velocity parameter. In our system the CB and the VB are formed from two different orbitals which have different chemical potential. Therefore, the dispersion relation for VB and CB near the Weyl point can be fitted with

$$E + \frac{0.39}{0.9} = \sqrt{1700(k - 0.051)^2 + 1.4(k - 0.051) + 0.149}$$

and

$$E - \frac{0.435}{0.89} = -\sqrt{4300(k - 0.051)^2 + 3.8(k - 0.051) + 0.147}$$

as shown in Fig. 4 a. We notice that crossing point is symmetric about the $\Gamma$ point and spin up and down channel of the band is degenerate in absence of the SOC. Therefore, this system preserves the both time reversal and inversion symmetry. The crossing points acts as source or sink of the Berry curvature. The Berry curvature calculated using Vaspberry shown in inset Fig. 4 b. The Berry curvature have highest value near one crossing point whereas it lowest value near the second crossing points, the direction of curvature is shown with arrow. In Fig. 5 projected density of states (PDOS) are shown for four different pressures, and the Bi and Se $p$ bands are marked separately. The contribution of Bi-$p$ band is higher near the $E_f$ in the CB than the Se-$p$ band, whereas in VB Se-$p$ band has higher contribution. At low pressure $P < 7.3$ GPa there is no density of states at $E_f$, and PDOS at $E_f$ increases with $P$, large PDOS can be seen at $P = 33.4$ GPa.
FIG. 3. (Color online) Figure showing the variations in band structures with the exertion of pressure. We observe the bands at Γ point denoted by G approaching each other and finally interpenetrating beyond the critical pressure to show the Weyl semimetal states.

FIG. 4. (Color online) Figure showing the emergence of Weyl states in Bi$_2$Se$_3$. Panel (a) shows the atom resolved band structure showing the Weyl points and the band inversion around the Fermi energy at a Pressure of 24.6GPa. Panel (a) also shows the bands near the band dispersion fitted to Eqs [1] and [2] corresponding to band dispersions for Weyl semimetals. The fitting is shown with bold lines corresponding to the atom resolved band structure. Panel (b) shows the Plot of Berry Curvature which shows the distinctive case of Weyl semimetals.

IV. EFFECT OF DOPING

In this section we discuss the effect of doping Bi$_2$Se$_3$ with a rare earth element Gd. The system can be doped either by the substituting Bi with Gd, or intercalating Gd between the QLs of Bi$_2$Se$_3$. Intercalating one Gd per unit cell gives rise to a doping fraction of 16.67% whereas substituting one Bi with Gd per unit cell gives rise to
FIG. 5. (Color online) Figure showing the variations in Projected density of states (PDOS) with the exertion of pressure. The energy is scaled with respect to Fermi energy. The red lines represent Bi p contribution while the blue lines represent Se p contribution.

a doping fraction of 20%. To our surprise the two different methods of doping, with similar doping fractions, resulted in two completely different electronic ground states. The highest valence and the lowest conduction bands are shown in Fig. 6a for pure, substituted and intercalated Gd in Bi$_2$Se$_3$ system. On substituting Bi with Gd, there is an increase in the split between the valence band maxima and conduction band minima, and hence the direct band gap increases to 0.5eV. The intercalation of Gd shifts the entire band structure to a lower energy in such a way that we now have a partially occupied conduction band, and a fully occupied VB as shown in Fig. 6(a), and therefore it is a wide band metal. The intercalated Gd induces rearrangement of energy bands which leads to band inversion below $E_f$, however, it is different from the pressure induced inversion. The band inversion below $E_f$ is shown in the circle in Fig. 6(a). In this case the up and down spin band split due to internal magnetic field induced by Gd atoms. Therefore the resulting time reversal symmetry is not preserved. The upper band is contributed from the Bi-band whereas the lower band contributed by Se atoms. Thus we observe a time reversal symmetry broken Weyl state whose existence has been discussed in literature.

The total DOS for three different cases pure, substituted and intercalated Bi$_2$Se$_3$ are shown in Fig. 6b, and we note that intercalation of Gd can lead to finite density of states at $E_f$ which leads to an insulator to metal transition. The large DOS comes from Gd f orbitals which are half filled and have high spin splitting. The rest of the DOS has usual contributions from Bi and Se p orbitals with some mixing with filled Gd d orbitals. The contribution to DOS at the Fermi in case of Gd intercalated Bi$_2$Se$_3$ is from the Bi p bands which is the partially filled conduction band. It is also to be noted that although the direct band gap changes in case of substitutional doping from pure Bi$_2$Se$_3$, the integrated band gap does not undergo any substantial change as observed from the total DOS.

The magnetic properties of the system under the influence of the dopant atom changes significantly. The substitutional doping gives rise to a AFM ordering consistent with earlier results. We find a similar AFM ordering between intercalated Gd atoms, as shown in Fig. 7. The large magnetic moment of $\sim 7 \mu_B$ on Gd which is consistent with literature. The large magnetic moment on Gd induces a small moment of $\sim 0.2 \mu_B$ on Se. The large magnetic moment may be because of larger exchange splitting compared to the crystal field splitting, in this case, the f-orbitals likely to be occupied by elec-
V. SUMMARY AND CONCLUSION

In our ab initio DFT study we note that bulk Bi$_2$Se$_3$ shows a tunable topological transition with the application of hydrostatic pressure and doping by rare earth elements. Upon application of hydrostatic pressure bulk Bi$_2$Se$_3$ shows a topological transition from a surface states driven topological insulator to a Weyl semimetal in bulk for $P > P_c$, and the topological transition may be correlated with structural phase transition from a layered to 3D material. For $P > P_c$, Se-p band and Bi-p band shows band inversion and these two bands cross at two points, $\pm k$ points or Weyl points around the $\Gamma$ point at the Fermi-energy. There is no spin-splitting at these crossing points, and $E_{\uparrow}(k) = E_{\downarrow}(-k)$. We notice that crossing points shifts to higher momentum $k$ for larger $P$, and the DOS at the Fermi-energy have finite value at large $P$.

We have also shown that a topological transition may also be achieved by doping. Our DFT calculations show that intercalating a rare earth element, Gd, between the QL has very different effects from the conventional methods of substitutional doping. While substitution leads to a larger direct band gap, intercalation leads to a metallic state with a large band width, and presence of Weyl points below the $E_F$, however, both cases of doping induces anti-ferromagnetic ordering in the system. We also note an induced magnetism in the system owing to the large magnetic moment on the rare earth dopant Gd atom.

The anti-ferromagnetic metallic state is particularly important for spintronics based application which may be driven in this material. This anti-ferromagnetic metallic state arises in case of intercalation of Gd between the QLs, and could be of immense importance in spintronics based applications. Anti-ferromagnetic metals have primarily been seen as exotic electronic structure states. Our study opens up new application possibilities in this 3D topological material, and most importantly shows the emergence of Weyl semimetal state in the Bi$_2$Se$_3$ family of materials by application of pressure which may be easily verified experimentally. Similar experiments may also be carried out with other materials in this class like Sb$_2$Te$_3$, Bi$_2$Te$_3$, and Bi$_2$Se$_3$.

We hope our study motivates further theoretical and particularly experimental studies to explore the tunable topological transitions, particularly in the search for Weyl semimetals, with associated magnetism in TIs both from the perspective of understanding of exotic states and device applications as well.

ACKNOWLEDGMENTS

The authors thank DST India for the funding and also computational facilities at S. N. Bose National Centre for Basic Sciences, Kolkata, provided by the Thematic Unit of Excellence on Computational Materials...
Science. MK thanks DST India for a Ramanujan Fellowship SR/S2/RJN-69/2012. HB thanks the Austrian Science Fund (FWF), for funding through START project Y746, and DST India for funding support during execution of the project. SKS thanks DST-INSPIRE for financial support. HB acknowledges useful discussions with Dr. Sudipta Kanungo and Dr. Oindrila Deb.

### VI. APPENDIX

#### TABLE I. Table showing change in lattice parameters with exertion of hydrostatic pressure

| P(GPa) | 0   | 5.5 | 10  | 16.4 | 24.6 | 33.4 |
|--------|-----|-----|-----|------|------|------|
| a (Å)  | 4.142 | 4.084 | 4.008 | 3.913 | 3.810 | 3.658 |
| b (Å)  | 4.142 | 4.084 | 4.008 | 3.913 | 3.810 | 3.658 |
| c (Å)  | 28.637 | 27.726 | 27.062 | 26.667 | 26.365 | 27.067 |
| c/a    | 6.914 | 6.788 | 6.752 | 6.816 | 6.919 | 7.398 |

#### TABLE II. Table showing change in bond angle and bond length with exertion of hydrostatic pressure (Note: Se1 is at the edge of the QL and Se2 is inside QL for pure Bi2Se3).

| P(GPa) | 0   | 5.5 | 10  | 16.4 | 24.6 | 33.4 |
|--------|-----|-----|-----|------|------|------|
| $d_{Bi-Se1}$ (Å) | 2.86 | 2.84 | 2.81 | 2.78 | 2.74 | 2.71 |
| $d_{Bi-Se2}$ (Å) | 3.07 | 3.03 | 2.98 | 2.92 | 2.87 | 2.82 |
| $\angle Se1-Bi-Se1$ | 92.61 | 91.91 | 90.82 | 89.41 | 88.09 | 84.0 |
| $\angle Se2-Bi-Se2$ | 84.98 | 84.74 | 84.6 | 83.89 | 83.27 | 80.75 |
| $\angle Se1-Se2$ | 91.13 | 91.6 | 92.2 | 93.17 | 94.19 | 97.22 |

* h.banerjee10@gmail.com
1 J. Moore, Nature Physics 5, 378 (2009)
2 J. E. Moore, Nature 464, 194 (2010)
3 C. Nayak, S. H. Simon, A. Stern, M. Freedman, and S. Das Sarma, Rev. Mod. Phys. 80, 1083 (2008)
4 T. Yokoyama and S. Murakami, Physica E: Low-dimensional Systems and Nanostructures 55, 1 (2014)
5 Y. Fan and K. L. Wang, SPIN 06, 1640001 (2016), https://doi.org/10.1142/S2010324716400014
6 M. He, H. Sun, and Q. L. He, Frontiers of Physics 14 (2019), 10.1007/s11467-019-0893-4
7 M. Z. Hasan and C. L. Kane, Rev. Mod. Phys. 82, 3045 (2010)
8 M. Z. Hasan and J. E. Moore, Annual Review of Condensed Matter Physics 2, 55 (2011), https://doi.org/10.1146/annurev-conmatphys-062910-140432
9 C. L. Kane and E. J. Mele, Phys. Rev. Lett. 95, 146802 (2005)
10 X. Chen, Z.-X. Liu, and X.-G. Wen, Phys. Rev. B 84, 235141 (2011)
11 R. Singh, V. K. Gangwar, D. D. Daga, A. Singh, A. K. Ghosh, M. Kumar, A. Lakhani, R. Singh, and S. Chatterjee, Applied Physics Letters 112, 102401 (2018)
12 F. Pollmann, E. Berg, A. M. Turner, and M. Oshikawa, Phys. Rev. B 85, 075125 (2012)
13 J. Betancourt, S. Li, X. Dang, J. D. Burton, E. Y. Tsymbal, and J. P. Velev, Journal of Physics: Condensed Matter 28, 395501 (2016)
14 W. Zhang, R. Yu, H.-J. Zhang, X. Dai, and Z. Fang, New Journal of Physics 12, 065013 (2010)
15 H. Zhang, C.-X. Liu, X.-L. Qi, X. Dai, Z. Fang, and S.-C. Zhang, Nature Physics 5, 438 (2009)
16 J. G. Checkelsky, Y. S. Hor, R. J. Cava, and N. P. Ong, Phys. Rev. Lett. 106, 196801 (2011)
17 J. Y. Park, G.-H. Lee, J. Jo, A. K. Cheng, H. Yoon, K. Watanabe, T. Taniguchi, M. Kim, P. Kim, and G.-C. Yi, 2D Materials 3, 035029 (2016)
18 Y. Xia, D. Qian, D. Hseh, L. Wray, A. Pal, H. Lin, A. Bansil, D. Grauer, Y. S. Hor, R. J. Cava, and M. Z. Hasan, Nature Physics 5, 398 (2009)
19 O. Chiatti, C. Riha, D. Lawrenz, M. Busch, S. Das Sarma, J. Sánchez-Barriga, A. Mogilatenko, L. V. Yashina, S. Valencia, A. A. Únal, O. Rader, and S. F. Fischer, Scientific Reports 6, 27483 (2016)
20 Y. Zhang, K. He, C.-Z. Chang, C.-L. Song, L.-L. Wang, X. Chen, J.-F. Jia, Z. Fang, X. Dai, W.-Y. Shan, S.-Q. Shen, Q. Niu, X.-L. Qi, S.-Y. Zhang, X.-C. Ma, and Q.-K. Xue, Nature Physics 6, 584 (2010)
21 A. Saha and A. M. Jayannavar, Resonance 22, 787 (2017)
22 A. Bera, K. Pal, D. V. Muthu, U. V. Waghmare, and A. K. Sood, J Phys Condens Matter. 28, 105401 (2016)
23 S. M. Young, S. Chowdhury, E. J. Walter, E. J. Moore, C. L. Kane, and A. M. Rappe, Phys. Rev. B 84, 085106 (2011)
24 W. Liu, X. Peng, C. Tang, L. Sun, K. Zhang, and J. Zhong, Phys. Rev. B 84, 245105 (2011)
25 A. Polian, M. Gauthier, S. M. Souza, D. M. Trichès, J.-a. Cardoso de Lima, and T. A. Grandi, Phys. Rev. B 83, 113106 (2011)
26 J. J. Hamlin, J. R. Jeffries, N. P. Butch, P. Syers, D. A. Zocco, S. T. Weir, Y. K. Vohra, J. Paglione, and M. B. Maple, Journal of Physics: Condensed Matter 24, 035602 (2011)
27 R. Vilaplana, D. Santamaria-Pérez, O. Gomis, F. J. Manjón, J. González, A. Segura, A. Muñoz, P. Rodríguez-Hernández, E. Pérez-González, V. Marín-Borrás, V. Muñoz Sanjose, C. Drasler, and V. Kucuk, Phys.
M. Bianchi, R. C. Hatch, Z. Li, P. Hofmann, F. Song, J. Mi, B. B. Iversen, Z. M. Abd El-Fattah, P. López, L. Zhou, A. A. Khajetoorians, J. Wiebe, R. Wiesendanger, and J. W. Wells, ACS Nano 6, 7009 (2012)

S.-W. Kim and M.-H. Jung, AIP Advances 8, 101319 (2018)  https://doi.org/10.1063/1.5042494

J. Kim, K. Lee, T. Takabatake, H. Kim, M. Kim, and M.-H. Jung, Scientific Reports 5, 10309 (2015)

Y. Wang, P. Deorani, K. Banerjee, N. Koirala, M. Brahlek, S. Oh, and H. Yang, Phys. Rev. Lett. 114, 257202 (2015)

C. H. Li, O. M. J. van ‘t Erve, J. T. Robinson, Y. Liu, L. Li, and B. T. Jonker, Nature Nanotechnology 9, 218 (2014)

Y. Ando, T. Hamasaki, T. Kurokawa, K. Ichiba, F. Yang, M. Novak, S. Sasaki, K. Segawa, Y. Ando, and M. Shiroyaishi, Nano Lett. 14, 6226 (2014)

Y. Yang, Z. Xu, L. Sheng, R. Shen, and D. Y. Xing, Applied Physics Letters 99, 182101 (2011)

K. Kirshenbaum, P. S. Syers, A. P. Hope, N. P. Butch, J. R. Jeffries, S. T. Weir, J. J. Hamlin, M. B. Maple, Y. K. Vohra, and J. Paglione, Phys. Rev. Lett. 111, 087001 (2013)

Z. Yu, L. Wang, Q. Hu, J. Zhao, S. Yan, K. Yang, S. Sino-Merk, G. Gu, and H.-k. Mao, Scientific Reports 5, 15939 (2015)

M. Yang, Y. Z. Luo, M. G. Zeng, L. Shen, Y. H. Lu, J. Zhou, S. J. Wang, I. K. Sou, and Y. P. Feng, Phys. Chem. Chem. Phys. 19, 29372 (2017)

N. P. Armitage, E. J. Mele, and A. Vishwanath, Rev. Mod. Phys. 90, 015001 (2018)

F. Arnold, M. Naumann, S.-C. Wu, Y. Sun, M. Schmidt, H. Borrman, C. Felser, B. Yan, and E. Hassinger, Phys. Rev. Lett. 117, 146401 (2016)

F. Arnold, C. Shekhar, S.-C. Wu, Y. Sun, R. D. dos Reis, N. Kumar, M. Naumann, M. O. Ajesh, M. Schmidt, A. G. Grushin, J. H. Bardarson, M. Baenitz, D. Sokolov, H. Borrmann, M. Nicklas, C. Felser, E. Hassinger, and B. Yan, Nature Communications 7, 11615 (2016)

G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996)

P. E. Blöchl, Phys. Rev. B 50, 17953 (1994)

J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)

S. Pakdel, M. Pourfath, and J. J. Palacios, Beilstein journal of nanotechnology 9, 1015 (2018), 29719753[pmid].

G. Huber, K.P.; Herzberg, Molecular Spectra and Molecular Structure. , 8 (1979)

T. Fukui, Y. Hatsugai, and H. Suzuki, Journal of the Physical Society of Japan 74, 1674 (2005).

https://doi.org/10.1143/JPSJ.74.1674

A. A. Zyuzin, S. Wu, and A. A. Burkov, Phys. Rev. B 85, 165110 (2012)

L. Smekal, Y. Mokrousov, B. Yan, and A. H. MacDonald, Nature Physics 14, 242 (2018)