Strain-induced quantum topological phase transitions in Na₃Bi

Dexi Shao¹, Jiawei Ruan¹, Juefei Wu¹, Tong Chen¹, Zhaopeng Guo¹,
Haijun Zhang¹,², Jian Sun¹,² * Li Sheng¹,², and Dingyu Xing¹,²

¹National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, China
²Collaborative Innovation Center of Advanced Microstructures, Nanjing 210093, China

Strain can be used as an effective tool to tune the crystal structure of materials and hence to modify their electronic structures, including topological properties. Here, taking Na₃Bi as a paradigmatic example, we demonstrated with first-principles calculations and k · p models that the topological phase transitions can be induced by various types of strains. For instance, the Dirac semimetal phase of ambient Na₃Bi can be tuned into a topological insulator (TI) phase by uniaxial strain along the ⟨100⟩ axis. Hydrostatic pressure can let the ambient structure transfer into a new thermodynamically stable phase with Fm3m symmetry, coming with a perfect parabolic semimetal having a single contact point between the conduction and valence bands, exactly at Γ point on the Fermi level like α-Sn. Furthermore, uniaxial strain in the ⟨100⟩ direction can tune the new parabolic semimetal phase into a Dirac semimetal, while shear strains in both the ⟨100⟩ and ⟨111⟩ directions can take the new parabolic semimetal phase into a TI. k · p models are constructed to gain more insights into these quantum topological phase transitions. At last, we calculated surface states of Fm3m Na₃Bi without and with strains to verify these topological transitions.

I. INTRODUCTION

Due to the inspiration from fundamental physics and interest in exotic properties for applications, new topological materials and phases with non-trivial band topology, such as topological insulators (TIs), topological metals/semmetals and topological superconductors, attracted tremendous attention in the past decade.¹⁻⁴ The non-trivial states are usually protected by certain symmetries, such as time-reversal symmetry (TRS), crystalline symmetry including inversion symmetry (IS). Among these topological states, TRS-protected surface states were first predicted in 1987⁵ to occur in quantum wells of HgTe sandwiched between CdTe and were successfully observed in experiments in 2006⁶. In 3D TIs, the surface state is actually a new type of two-dimensional (2D) massless electron gas, with its spin locked to its momentum ⁷,⁸. These robust metallic surface states differ TIs from normal insulators and make TIs greatly attractive.

Compared with TIs indexed by Z₂, topological semimetals, in which band crossings appear at Fermi level in a reduced dimension, have attracted more attention because they may supply platforms to investigate new types of fermion-like excitations, including Dirac fermions⁹,¹⁰, Weyl fermions¹¹⁻¹⁴ and nodal lines¹⁵⁻²⁰, etc. Among them, the earliest example may be the 2D Dirac semimetal – graphene²¹,²². Interestingly, later works show that the surface states in 3D TIs also present 2D massless Dirac-like dispersions. Among many candidates with Dirac-like dispersions have been reported⁹,¹⁰,²³⁻²⁵, Cd₃As₂ and Na₃Bi are particularly attractive 3D Dirac semimetals with their Dirac points locating exactly at the Fermi level. Featured by 3D Dirac points in the bulk and Fermi arcs on the surface⁹,¹⁰,²³⁻²⁵, 3D Dirac semimetals have recently been identified experimentally in Cd₃As₂²⁶⁻²⁸ and Na₃Bi systems³¹,³².

Na₃Bi was predicted to be a 3D bulk Dirac semimetal (DSM)⁹ and verified later by experiments³¹. This topological Dirac fermion in Na₃Bi is protected by TRS and IS together with R₃z symmetry. It is known that breaking of the R₃z symmetry, for example 1% compression along the y axis, will change the system into a TI with Z₂ = 1⁻¹². After the predictions of Na₃Bi to be a 3D Dirac semimetal, large efforts were invested to study this interesting system, for instance, Fermi arc surface states³², quantum oscillations³¹, evidence for the chiral anomaly⁴⁴, magnetoresistance⁶⁵, etc. As we know, alkali pnictides A₃B (A = alkali metal, B = pnictide) usually crystalline into two different structures at ambient pressure: the hexagonal P6₃/mmc phase (e.g., K₃Bi and Rb₃Bi) and the cubic Fm3m phase (e.g., Li₃Bi and Cs₃Bi)⁶⁶. Actually, phonon spectra of P6₃/mmc phase of Na₃Bi show negative frequencies, which means this phase should not be dynamically stable, Cheng et al.³⁷ reported that the ground state of Na₃Bi at ambient pressure could be a P3c1 (or so-called hP24) phase, which is a distorted superlattice version of the P6₃/mmc phase. And this P3c1 phase also exhibits features of 3D Dirac semimetal.

Pressure and strain have been used as effective methods to modify the topological properties of materials, for instance, in graphene³⁸, BiTeF³⁹, HgTe-class⁴⁰, Cd₃As₂⁴¹⁻⁴₃, TaAs⁴⁴, ZrTe₂⁴⁵, WTe₂⁴⁶, SnTe⁴⁷, TaB⁴⁸, etc. The work by Cheng et al.⁴⁹,⁵⁰ showed that Na₃Bi would undergo a pressure-induced structural phase transition from the P3c1 (hP24) phase to a cubic Fm3m (cF16) phase at pressure of about 0.8 GPa, which is in good agreement with previous experimental findings⁵¹,⁵². The transition pressure for Na₃Bi is such low, which means compressive strain has a large effect on the structure of this system. Previous work⁵⁰ reported that shear strain along ⟨100⟩ axis can develop the cubic phase of Na₃Bi into a TI. However, whether or how different type of strain will affect the topological properties of Na₃Bi and detailed analysis with model Hamiltonian...
still remains an open question. In this work, we have studied effects of several different strains on Na₃Bi, including uniaxial tensile/compressive strain and shear strain in different directions. We find that uniaxial strain on Na₃Bi in the space group of Pm3c1 at ambient pressure can induce a topological phase transition from Dirac semimetal to TI. With the help of Luttinger Hamiltonian⁵⁴, we also find the Fm3m phase to be a perfect parabolic semimetal. We then impose a uniaxial strain on the Fm3m lattice and find it will open a gap at the Γ point and induce a Dirac crossing near the Γ. Furthermore, with the help of a the lattice parameters of Na₃Bi are showed in Table. I.

II. METHODOLOGY AND THE DETAIL

Ab initio random structure searching⁵⁴,⁵⁵ is applied for crystal structure searching under pressure. Structure optimization is performed using projector augmented wave (PAW) potential⁵⁶ with the Perdew-Burke-Ernzerhof⁵⁷ generalized gradient approximation (PBE-GGA) exchange-correlation functional implemented in the Vienna ab initio simulation package (VASP)⁵⁸ in the framework of density functional theory (DFT). The plane wave cutoff is set to 850 eV, structure relaxation is carried out until all of the atomic forces on each ion is less than 0.0025 eV/Å. Electronic band structures calculations are carried out using full-potential linearized augmented plane-wave method implemented in the WIEN2k⁵⁹ package. SOC is taken into account self-consistently. 21 × 21 × 21 k-mesh is used as the period boundary condition for electronic structure calculation under ambient and high pressure.

III. THE ELECTRONIC STRUCTURES OF P3c1 PHASE UNDER UNIAXIAL STRAIN

A recent work reveals that the zero-pressure ground state of Na₃Bi should be the P3c1 phase which presents the features of Dirac semimetal⁵⁷. The crystal structures of the P3c1 phase are shown in Fig. 1, and the corresponding lattice parameters are shown in Table. I.

There are 24 atoms in one unit cell of the P3c1 phase which occupy 4 nonequivalent positions. We sign the atoms locate at these nonequivalent positions with Na1, Na2, Na3 and Bi, respectively, as shown in Fig. 1 (a). The band structure with SOC for the P3c1 phase Na₃Bi is shown in Fig. 2(b), the result is similar to earlier work by Cheng et al.⁵⁷ We impose a uniaxial tensile strain along the x axis and meanwhile a compressed strain along the y axis to keep the volume unchanged. As shown in Fig. 2(a), this operation or vice versa, breaks the R₃ symmetry in the P3c1 phase and changes the space group of the structure from P3c1 to P1. We take 2% uniaxial strain as an example here, and the resulting band structure with SOC is shown in Fig. 2(c). From the band structure we can assert that it is an insulator directly. Using the method by Fu and Kane⁶⁰, we can easily calculate the Z₂ index by multiplying all the parities for all the occupied bands at all time-reversal-invariant momenta (TRIMs). The results are shown in Table. II, which indicates Z₂ = (1, 111) for this system. This shows that uniaxial strain will induce a topological phase transition from Dirac semimetal to TI in the P3c1 phase.

![Image](https://example.com/image.png)

FIG. 1. (a) Crystal structure of Na₃Bi at the ambient pressure with P3c1 symmetry. Na1, Na2 and Na3 atoms occupy the 2a(0,0,0), 4d(0,0.0,200) and 12g(0.354,0.319,0.083) sites, respectively, while Bi atoms lie at the 6f(0.337,0,0) site. (b) Crystal structure of Na₃Bi at 1 GPa with Fm3m symmetry. Na1 and Na2 atoms occupy the 4a(0,0,0), 8c(0.5,0,0) sites while Bi atoms stay at the 4b(0.0,0.5) site.

| TABLE I. Lattice parameters of Na₃Bi at the ambient pressure with P3c1 symmetry and 1 GPa with Fm3m symmetry. |
|-----------------|-----------------|-----------------|-----------------|
| phase pressure  | a (Å)           | α (°)           | γ (°)           |
| Na₃Bi           | 0.9459          | 90              | 120             |
| Fm3m            | 1.7458          | 90              | 90              |

TABLE II. The product of the parities for all the occupied bands at the eight TRIMs for the P3c1 phase of Na₃Bi with uniaxial strain.

| TRIM | Γ | 3M | 3L | A | total |
|------|---|----|----|---|------|
| Parity | + | –  | –  | –  | –    |

[References]

⁵⁴ Cheng et al., 2017
⁵⁵ Perdew et al., 1986
⁵⁶ Perdew et al., 1992
⁵⁷ Luttinger, 1956
⁵⁸ Blöchl, 1994
⁵⁹ Kresse and Hafner, 1993
⁶⁰ Fu and Kane, 2007
IV. THE ELECTRONIC STRUCTURES OF THE HIGH-PRESSURE FM3M PHASE

Crystal structure searches and thermodynamic calculations afterwards show that a cubic phase in the space group of FM3m becomes more stable than the ambient P3c1 phase under critical pressure around 0.8 GPa\(^50\).

For the FM3m phase, there are 4 atoms occupying 3 nonequivalent positions in one primitive cell as shown in Fig. 1(b). The 4 atoms can be signed as Na\(_1\), Na\(_1\)' , Na\(_2\), and Bi. Among them, Na\(_1\) and Na\(_1\)' are equivalent as a result of IS.

The detailed structural parameters of the FM3m phase are listed in Table. I. And its electronic band structures without and with SOC are illustrated in Fig. 3(a) and Fig. 3(b), similar to the results by by Cheng et al.\(^49\).

The most interesting feature one can find in the band structures with and without SOC, as shown in Fig. 3 (a) and (b), is that there is only one touching point between the valence and conduction bands, which exactly locates at Γ point on the Fermi level. Detailed first-principle calculations without SOC indicates that this touching point is a triply degenerate point contributed mainly by Bi-6p\(_z\) orbitals, and the wave functions of low-energy states around the touching point mainly consist of Na-3s and Bi-6p\(_z\) orbitals. Due the fact that there are two Na\(_1\) atoms (signed with Na\(_1\) and Na\(_1\)' ), which are centrosymmetric connected to each other, thus we can construct bonding and antibonding states with definite parity from the s orbitals of Na\(_1\) and Na\(_1\)' atoms as follows:

\[
|\text{Na}^\pm, s > = \frac{1}{\sqrt{2}}(|\text{Na}_1; s > \pm |\text{Na}_1'; s >)
\]  

While there is only one atom for Na\(_2\) and Bi in the primitive cell, therefore, the parity of the orbits of Na\(_2\) and Bi atoms are only determined by their orbital angular quantum number themselves.

Taking SOC into consideration, spin and orbital angular momentum are coupled together, which generates a group of new eigenstates with certain total angular quantum numbers. We mark these new eigenstates as \(|S^\pm_{\text{Na}_1, 1/2}, \pm 1/2 >, |S^+_\text{Na}_2, 3/2, \pm 1/2 >, |S^+_\text{Bi}, 3/2, \pm 1/2 >, |P^-_{\text{Bi}, 1/2}, \pm 3/2 >, |P^-_{\text{Bi}, 1/2}, \pm 1/2 > and |P^-_{\text{Bi}, 1/2}, \pm 1/2 >\). Here \(S\) and \(P\) denote corresponding orbits consisting of the new eigenstates and the superscripts \(\pm\) represent the parities of corresponding eigenstates.

According to the analysis of irreducible representations and projected orbits, the touching point of the top of valence bands and the bottom of conduction bands (denoted as \(\Gamma^\pm\)) is mainly composed of \(|P^-_{\text{Bi}, 1/2}, \pm 3/2 >\) and \(|P^-_{\text{Bi}, 1/2}, \pm 1/2 >\) basis. We simplify the notation of these four basis as \(|J, j_z >\) with \(J = \frac{3}{2}\) and \(j_z = \pm \frac{3}{2}, \pm \frac{1}{2}\).

Take the time-reversal and point-group symmetries into consideration, a \(4 \times 4\) Luttinger Hamiltonian\(^53\) can exactly describe the \(\Gamma^\pm\) bands around the Γ point if we arrange the 4 basis in the order of \(|\frac{3}{2}, \frac{3}{2} >, |\frac{3}{2}, \frac{1}{2} >, |\frac{3}{2}, -\frac{1}{2} >, |\frac{3}{2}, -\frac{3}{2} >\), with the Hamiltonian given by

\[
H_{\text{Luttinger}}(\vec{k}) = \alpha_0 \vec{k}^2 I + \alpha_1 (\vec{k} \cdot \vec{J})^2 + \alpha_2 \sum_{i=1}^{3} k_i^2 J_i^2, \tag{2}
\]
where \( J_i (i = 1, 2, 3) \) are spin- \( \frac{3}{2} \) matrices and \( \alpha_i (i = 0, 1, 2) \) are parameters characterizing the band structures. These three parameters are determined as \( \alpha_0 \approx 205.3 \) \( \text{Å}^2\text{eV} \), \( \alpha_1 \approx -83.1 \) \( \text{Å}^2\text{eV} \), \( \alpha_2 \approx -22.5 \) \( \text{Å}^2\text{eV} \) by fitting the first-principle band structures around the \( \Gamma \) point. With this Luttinger Hamiltonian, we can nicely describe the unique parabolic dispersion near \( \Gamma \) at the Fermi level as shown in Fig. 3(c), which is quite different from the linear Dirac dispersions.

V. THE EFFECT OF DIFFERENT STRAIN ON THE HIGH-PRESSURE FM\( \bar{3} \)M PHASE

A. UNIAXIAL STRAIN ON the FM\( \bar{3} \)m PHASE

When we impose a uniaxial strain \( \epsilon \) along any orthogonal axis on the original FM\( \bar{3} \)m structure, it will change the symmetry of the crystal from space group FM\( \bar{3} \)m to \( I4/\overline{mmm} \). Here, to keep the volume of the cell invariable, when a tensile strain \( \epsilon \) is applied along the \( z \) axis, we add at the same time a compressive strain \( \frac{\sqrt{1+\epsilon}}{2} \) along the \( x \) and \( y \) axes, respectively. It is obvious that this operation changes the symmetry of the structure from FM\( \bar{3} \)m to \( I4/\overline{mmm} \) as well. The uniaxial compressive or tensile strain energy relative to the perfect FM\( \bar{3} \)m structure is shown in Fig. 4 (a), which indicates that the tensile strain somehow is easier to obtain than the compressive one in this system.

With this uniaxial strain operation, as shown in Fig. 6 (a), we can predict that the triply degenerate \( p_{x,y,z} \) orbits without SOC at \( \Gamma \) point will split into a non-degenerated \( p_z \) and a doubly degenerated \( p_{x,y} \) orbits due to the crystal-field splitting.

When SOC is considered, this uniaxial strain may lead to the appearance of a Dirac crossing near the \( \Gamma \) point.

In fact, the uniaxial strain changes the point group of the system from \( O_h \) to \( D_{4h} \), which also affects the \( \mathbf{k} \cdot \mathbf{p} \) Hamiltonian dramatically. As the permutation symmetry of \( x, y, z \) directions is no longer preserved, \( J_x, J_y, J_z \) is not convenient to be used as basis any more. Here we use the following \( \Gamma \) matrices:

\[
\Gamma_1 = \frac{1}{\sqrt{3}} \{ J_y, J_z \}, \quad \Gamma_2 = \frac{1}{\sqrt{3}} \{ J_z, J_x \}, \quad \Gamma_3 = \frac{1}{\sqrt{3}} \{ J_x, J_y \}
\]

\[
\Gamma_4 = \frac{1}{\sqrt{3}} (J_x^2 - J_y^2), \quad \Gamma_5 = J_z^2 - \frac{5}{4} J_x^2.
\]

(3)

while the other ten \( \Gamma \) matrices are given by \( \Gamma_{ab} = \frac{1}{3} [\Gamma_a, \Gamma_b] \). The coexistence of TRS and IS constrains that no \( \Gamma_{ab} \) terms exist in the model Hamiltonian. After a careful analysis of the symmetry and a tedious derivation, we can give the character table of the \( \Gamma \) matrices and the polynomials of momentum \( \mathbf{k} \) as shown in Table. III using the same basis functions above-mentioned.
Finally, from Table III, our model Hamiltonian yields as

\[ H = \sum_{\Gamma} f_i(\vec{k}) \Gamma_i = [a_0 + b_0(k_x^2 + k_y^2) + c_0k_z^2]\Gamma_0 + a_{12}(k_yk_z\Gamma_1 + k_xk_z\Gamma_2) + a_3k_xk_y\Gamma_3 + a_4(k_x^2 - k_y^2)\Gamma_4 + [a_5 + b_0(k_x^2 + k_y^2) + c_5k_z^2]\Gamma_5. \] (4)

The dispersion of above-mentioned model is \( E(\vec{k}) = f_0(\vec{k}) \pm \sqrt{f_1^2(\vec{k}) + f_2^2(\vec{k}) + f_3^2(\vec{k}) + f_4^2(\vec{k}) + f_5^2(\vec{k})} \) and both dispersions are doubly degenerated. As a result, a band crossing of this model requires \( f_1 = f_2 = f_3 = f_4 = f_5 = 0 \), i.e. \( k_z \neq 0 \cap k_x = k_y = 0 \cap a_5c_5 < 0 \). It means that we can always find a Dirac crossing along \( k_z \) direction when \( a_5c_5 < 0 \) stands, and the location of the crossing is \( \vec{k} = (0,0,\pm \sqrt{-\frac{a_5}{c_5}}) \). Otherwise, a gap near the \( \Gamma \) point induced by \( a_5\Gamma_5 \) will always preserve.

When the bands are gapped, the existence of both the TRS and IS in the uniaxial-strained \( \text{Fm3m} \) \( \text{Na}_3\text{Bi} \) enables us to calculate \( Z_2 \) using Fu and Kane's method. The results are listed in Table IV, which indicates \( Z_2 = (1,0,0) \).

Note that the \( Z_2 \) index remains unchanged when we tune any parameters in the above-mentioned model because band inversion between \( \Gamma \) and \( \Gamma \) cannot bring the parity inversion (the parities of both \( x,y \) bands at the eight \( \text{TRIMs} \) for the \( \text{Fm3m} \) phase of \( \text{Na}_3\text{Bi} \) under uniaxial strain along \( z \) axis)

TABLE III. The character table for the \( \text{Fm3m} \) phase of \( \text{Na}_3\text{Bi} \) under uniaxial strain along \( z \) axis.

| \( \Gamma \) | Representation | \( T \) | \( \vec{k} \) |
|---|---|---|---|
| \( \Gamma_0 = I \) | \( \Gamma_+^1 \) | + | \( k_x^2 + k_y^2 \) |
| \( \{\Gamma_1, \Gamma_2\} \) | \( \Gamma_+^3 \) | + | \( k_xk_y + k_yk_z \) |
| \( \Gamma_3 \) | \( \Gamma_+^4 \) | + | \( k_xk_y \) |
| \( \Gamma_4 \) | \( \Gamma_+^5 \) | + | \( k_x^2 - k_y^2 \) |
| \( \Gamma_5 \) | \( \Gamma_+^6 \) | + | \( k_x^2 + k_y^2 \) |

TABLE IV. The product of the parities for all the occupied bands at the eight TRIMs for the \( \text{Fm3m} \) phase of \( \text{Na}_3\text{Bi} \) under uniaxial strain along \( z \) axis.

| TRIM | \( \Gamma \) | 4N | 2X | M : total |
|---|---|---|---|---|
| Parity | - | + | + | + : - |

Here we give a qualitative explanation. Uniaxial strain along the \( z \) axis generates a perturbation \( H_{\text{strain;Na1;Na2}} = -g_{1,2}(J_x^2 - \frac{5}{4}) \). Here \( H_{\text{strain;Na1;Na2}} \) denotes the crystal perturbation on \( \text{Bi, p} > \) from the effect of the strain on \( \text{Na1 and Na2} \), respectively. From the unstrained structure in Fig. 6(a), we find that six \( \text{Na1} \) atoms around the body-centered \( \text{Bi} \) atom form an octahedron while eight \( \text{Na2} \) atoms form a cubic. We further consider the effect of the \( \text{Na1-octahedron and Na2-cubic} \) on \( \text{Bi, p} > \) by removing all the \( \text{Na2 or Na1 atoms} \), respectively. As the blue and the green lines shown in Fig. 6(d), first-principle calculations of these two different cases indicate that with the absence of \( \text{Na2-cubic}, g_1 < 0 \) \((g_1 > 0) \) corresponds to the tensile strain (the compressive strain); while we remove \( \text{Na2 cubic}, g_2 > 0 \) \((g_2 < 0) \) corresponds the tensile strain (the compressive strain). However, \( g_1 + g_2 \) is always less than 0 for both tensile and compressive strain, which means \( \text{Na1-octahedron effects Bi, p} \) more in the tensile strain case, while \( \text{Na2-cubic effects more in the compressed strain case.} \)
FIG. 6. (a) Schematic diagram of the Fm\overline{3}m phase with uniaxial strain. Six Na1 atoms (pink) next-nearest neighbour around the body-centered Bi (purple) form an octahedron while eight Na2 (yellow) nearest neighbour around form a cubic; (b) and (c) The band structures near Γ point of Na\textsubscript{3}Bi in the space group of I\textsubscript{4}/mmm which comes from uniaxial strain along z axis on the Fm\overline{3}m phase without and with spin orbital coupling. The red and blue lines correspond to CBM and VBM respectively. (d) The energy difference between |Bi, p_{x,y}> and |Bi, p_z> near the fermi level vs. uniaxial strains in the range of $-10\% \leq \epsilon \leq 10\%$ for the intact, Na1-absent and Na2-absent Na\textsubscript{3}Bi.

TABLE V. The product of the parities for all the occupied bands at eight TRIMs for the Fm\overline{3}m phase of Na\textsubscript{3}Bi with shear strain along (100) axis.

| TRIM | Γ | 2S | 2R | 2T | X ; | total |
|------|---|---|---|---|---|---|
| Parity | − | − | − | + | + ; | − |

B. SHEAR STRAIN ALONG the ⟨100⟩ DIRECTION ON the Fm\overline{3}m PHASE

Shear strain might have different effect on the electronic structures compared with tensile or compressive strain. If we impose a shear strain along ⟨100⟩ direction on the original Fm\overline{3}m structure, we will get a structure in the space group of I/mmm which belongs to the D\textsubscript{2h} point group. In fact, as shown in Fig. 7 (a), this operation only slightly changes one of the three lattice angles. The green line in Fig. 4 (b) shows how shear strain energy $E_{\text{ss}}$ varies with the angle parameter γ ranging from 85° to 95°. It seems that the shear strain costs a large mount of energy. Here we take the change of γ from 90° to 86° as an example. Electronic band structure shown in Fig. 7(b) indicates that the resulting structure is an insulator with a small gap of around 17 meV. The D\textsubscript{2h} point group ensures the existence of the inversion symmetry in the shear-strained structure, which enables us to calculate $Z_2$ by multiplying the parities for all the occupied Bloch states at the eight TRIMs using Fu and Kane’s method\textsuperscript{60}. The results are listed in Table. V, which clearly show $Z_2 = 1$. Thus shear strain along the ⟨100⟩ direction brings the system from a semimetal into a TI.

In fact, the shear strain changes the point group from O\textsubscript{h} to D\textsubscript{2h}, which also affects the $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian dramatically. After a careful analysis of the symmetry and a tedious derivation, one can give the character table of the Γ matrice and the polynomials of momentum $\mathbf{k}$ as shown in Table. VI.

TABLE VI. The character table for the Fm\overline{3}m phase of Na\textsubscript{3}Bi with shear strain along (100) axis.

| Γ | Representation | T | $\mathbf{k}$ |
|---|---|---|---|
| $\Gamma_0 = I$ | $\Gamma_0^+$ | + | 1, k\textsuperscript{2}, k\textsubscript{y}\textsuperscript{2}, k\textsubscript{z}\textsuperscript{2} |
| $\Gamma_1$ | $\Gamma_1^+$ | + | k\textsubscript{y}k\textsubscript{z} |
| $\Gamma_2$ | $\Gamma_2^+$ | + | k\textsubscript{x}k\textsubscript{y} |
| $\Gamma_3$ | $\Gamma_3^+$ | + | k\textsubscript{x}k\textsubscript{z} |
| $\Gamma_4$ | $\Gamma_4^+$ | + | 1, k\textsuperscript{2}, k\textsubscript{y}\textsuperscript{2}, k\textsubscript{z}\textsuperscript{2} |
| $\Gamma_5$ | $\Gamma_5^+$ | + | 1, k\textsuperscript{2}, k\textsubscript{y}\textsuperscript{2}, k\textsubscript{z}\textsuperscript{2} |
Finally, from Table VI, our model Hamiltonian yields

\[ H = \sum_{i=0}^{5} f_i(\vec{k}) \Gamma_i \]

\[ = \sum_{i=0,4,5} (a_i + b_{1x} k_x^2 + b_{1y} k_y^2 + b_{1z} k_z^2) \Gamma_i \]

\[ + c_1 k_y k_z \Gamma_1 + c_2 k_x k_z \Gamma_2 + c_3 k_x k_y \Gamma_3. \]

It’s clear that the band gap in the sheared structure comes from \( a_4 \Gamma_4 + a_5 \Gamma_5 \), which depends on the point group \( D_{2h} \) completely. Similarly, a band crossing of above-mentioned model requires \( f_1 = f_2 = f_3 = f_4 = f_5 = 0 \), i.e. \( k_\alpha = k_\beta = 0 \cap k_\gamma \neq 0 \cap \frac{a_4}{b_{4x}} = \frac{a_5}{b_{5x}} < 0 \). Here \( \alpha, \beta, \gamma \) is a permutation of \( \{x, y, z\} \). It means that we can find a Dirac crossing along \( k_\gamma \) direction only when \( \frac{a_4}{b_{4x}} = \frac{a_5}{b_{5x}} < 0 \) stands, and the location of the crossing is \( k_\alpha = k_\beta = 0, k_\gamma = \pm \sqrt{-\frac{2a_5}{b_{5x}}} \). However, from our ab initio calculations, a gap always exists when shear deformation along the \( \langle 100 \rangle \) axis (\( \gamma \)) is in the range of \( 85^\circ - 95^\circ \). In fact, \( \frac{a_4}{b_{4x}} = \frac{a_5}{b_{5x}} < 0 \) is a very rigorous condition, which can not be obtained without imposing other symmetries. Thus a gap near \( \Gamma \) will always occur. On the other hand, the \( Z_2 \) invariant remains unchanged because of the same reason discussed for the uniaxial-strained case. Therefore, the splitting of crystal field together with SOC generates \( a_4 \Gamma_4 \) and \( a_5 \Gamma_5 \) in the Hamiltonian, and results in the topological nontrivial band gap at \( \Gamma \) point.

**C. SHEAR STRAIN ALONG the \( \langle 111 \rangle \) DIRECTION ON the Fm3m PHASE**

Then we consider the case of shear strain along the body diagonal direction as Fig. 8(a) shows. This type of strain turns the space group of the structure from \( \text{Fm} \overline{3} \text{m} \) to \( \text{R} \text{3} \text{m} \) (belongs to the \( \text{D}_{3h} \) point group). In fact, this type of strain can also be obtained by changing the \( \alpha, \beta \) and \( \gamma \) by the same amplitude, which can be seen as a combination of shear strains along the \( \langle 100 \rangle \), \( \langle 010 \rangle \), \( \langle 001 \rangle \) directions. The red line in Fig. 4(b) shows how shear strain energy \( E_{\text{strain}}(\langle 111 \rangle) \) varies with the angle parameter \( \alpha = \beta = \gamma \) ranging from \( 85^\circ \) to \( 95^\circ \). Here we choose \( \alpha = \beta = \gamma = 92^\circ \) as an example.

The corresponding band structure shown in Fig. 8(b) indicates an insulator phase. Due to the preservation of IS, we calculate the product of the parities for the occupied bands at all the eight TRIMs, the result is shown in Table VII. Parity inversion at the \( \Gamma \) point leads to a nontrivial band topology with \( Z_2 = (1,0,0) \), which indicates that this \( \langle 111 \rangle \) sheared structure is a strong TI.

After similar analysis of the symmetry and derivation, we can give the character table of \( \Gamma \) matrices and the polynomials of momenta \( \vec{k} \) for the case of \( \langle 111 \rangle \) shear strain as Table. VIII shows. As a result, we can obtain the corresponding \( \vec{k} \cdot \vec{p} \) Hamiltonian as

\[ H = \sum_{i=0}^{5} f_i(\vec{k}) \Gamma_i \]

\[ = [a_0 + b_0(k_x^2 + k_y^2) + c_0 k_z^2] \Gamma_0 + a_{12} (k_y k_z \Gamma_1 + k_z k_x \Gamma_2) + b_{12}[-2k_x k_y \Gamma_1 + (k_z^2 - k_y^2) \Gamma_2] + a_{34}[2k_z k_x \Gamma_3 + (k_x^2 - k_y^2) \Gamma_4] + b_{34}[k_y k_z \Gamma_3 - k_x k_z \Gamma_4] + [a_5 + b_5 (k_x^2 + k_y^2) + c_5 k_z^2] \Gamma_5. \]

Similarly, a band crossing of this model requires \( f_1 = f_2 = f_3 = f_4 = f_5 = 0 \). It can be classified into two cases. (a) \( k_x = k_y = 0 \cap k_z \neq 0 \cap a_5 c_5 < 0 \), (b) \( \frac{a_4}{b_{12}} = -\frac{a_3}{a_{12}} \cap k_z \neq 0 \cap a_5 b_5 < 0 \cap a_5 c_5 < 0 \). In the case of (b), if \( \frac{a_4}{b_{12}} > 0 \), we can define \( l = \sqrt{-\frac{a_4}{b_{12}} c_5} \), then six Dirac points locating at \( \pm l, \pm \frac{a_4}{b_{12}} l, \pm \frac{a_3}{a_{12}} l \) and \( \pm \frac{a_5}{l}, \pm \frac{a_4}{b_{12}} l, \pm \frac{a_3}{a_{12}} l \) can be found. It’s obvious that they are related to each other by \( R_3 \) symmetries. However, it should be noted that the condition of \( a_4 \) in case (b) is very rigorous and can not be obtained without other symmetries, i.e., case (a) is a unique condition for a stable DSM. Thus, as discussed in the case of uniaxial strain, this system belongs to TI when \( a_5 c_5 > 0 \), while it transforms into a DSM only in the case of \( a_5 c_5 < 0 \). As a
result, this system have the same phase diagram as shown in Fig. 5. Similar to the shear strain along (100) direction case, from our ab initio calculations, a gap always exists when shear deformation along the the (111) axis ($\alpha = \beta = \gamma$) is in the range of $85 - 95^\circ$. Which indicates that $a_3c_5 > 0$ always stands for this shear strain. Due to the similar reason as discussed in the case of uniaxial strain, the gap induced by $a_3\Gamma_4$ term from $D_{3d}$ symmetry will always remain and the $Z_2$ will not change.

VI. SURFACE STATES OF THE FM$\bar{3}$M PHASE WITHOUT AND WITH STRAIN

Exotic topological surface states is an important property to identify various topological phases. Based on the tight-binding model constructed with MLWFs (maximally localised Wannier functions) method$^{61-63}$, we have calculated the projected surface states of the FM$\bar{3}$m Na$_3$Bi without strain and with different type of strains, as shown in Fig. 9. As showed in Fig. 9(a), no topological protected surface states can be found easily in the FM$\bar{3}$m Na$_3$Bi without strain. When we impose a uniaxial strain on FM$\bar{3}$m Na$_3$Bi, a Dirac crossing appears near the $\Gamma$ point in the bulk band structure. And the corresponding non-trivial surface states connecting the Dirac point also emerges, as showed in Fig. 9(b). As discussed above and showed in Fig. 9(c) and Fig. 9(d), shear strains along the (100) and (111) directions induce the original system into TIs, nontrivial metallic surface states can be found in the gap.

VII. CONCLUSION

In conclusion, with first-principle calculations we investigate the effect of stress/strain on Na$_3$Bi, a native 3D Dirac semimetal, and find strains have large effects on the topological band structures of this system. We apply a uniaxial strain to break the $R_{3z}$ symmetry on the ambient $P3c1$ phase and find that this strain tunes Na$_3$Bi into a TI with a topological nontrivial gap at $\Gamma$ point. Ab initio calculations show that the high pressure FM$\bar{3}$m phase is a new type of semimetal with the unique parabolic touching point at $\Gamma$ point on the Fermi level, which can be well described by a Luttinger Hamiltonian. According to our calculations, uniaxial strain along the (001) direction can tune the high pressure FM$\bar{3}$m Na$_3$Bi from the parabolic semimetal into a DSM, while shear strain along both the (100) and (111) directions can tune the high pressure FM$\bar{3}$m phase from the parabolic semimetal into a TI. To gain more insights on these quantum phase transition from strain, we derive three $\mathbf{k} \cdot \mathbf{p}$ models for the FM$\bar{3}$m phase and with all kinds of shear strains. It is obvious that SOC together with the splitting of crystal field from strains we imposed play key roles for the topological phase transitions in Na$_3$Bi. In the end, we calculated surface states of FM$\bar{3}$m Na$_3$Bi without strain and with different types of strains to verify these topological transitions. Different substrate might be used to introduce strain on samples grew on them, which might be used to examine the topological phase transitions studied in this work.

VIII. ACKNOWLEDGMENTS

We thank the fruitful discussions with Huaqiang Wang, Mengnan Chen, Feng Tang and Yongping Du. This work is supported by the MOST of China (Grant Nos: 2016YFA0300404, 2015CB921202), the National Natural Science Foundation of China (Grant Nos: 51372112, 11574133 and 11674165), NSF Jiangsu province (No. BK20150012), the Science Challenge Project (No. TZ2016001), the Fundamental Research Funds for the Central Universities (No. 20150012), the Science Challenge Project (No. TZ2016001), the Fundamental Research Funds for the Central Universities (No. 201414380068/1-1), Special Program for Applied Research on Super Computation of the NSFC-Guangdong Joint Fund (the second phase), and Open Fund of Key Laboratory for Intelligent Nano Materials and Devices of the Ministry of Education (INMD-2016M01). Part of the calculations were...
performed on the supercomputer in the HPCC of Nanjing University and "Tianhe-2" at NSCC-Guangzhou.

* To whom correspondence should be addressed. E-mail: jiansun@nju.edu.cn

1 M. Z. Hasan and C. L. Kane, Rev. Mod. Phys. 82, 3045 (2010).
2 X.-L. Qi and S.-C. Zhang, Rev. Mod. Phys. 83, 1057 (2011).
3 A. A. Burkov, M. D. Hook, and L. Balents, Phys. Rev. B 84, 235126 (2011).
4 H. Weng, X. Dai, and Z. Fang, J. Phys.: Cond. Matter 28, 303001 (2016).
5 O. Pankratov, S. Pakhmov, and B. Volkov, Solid State Commun. 61, 93 (1987).
6 B. A. Bernevig, T. L. Hughes, and S.-C. Zhang, Science 314, 1757 (2006).
7 D. Hsieh, Y. Xia, D. Qian, L. Wray, J. H. Dil, F. Meier, J. Osterwalder, L. Patthey, J. G. Checkelsky, and N. P. Ong, Nature 460, 1101 (2009).
8 H. Zhang, C. X. Liu, X. L. Qi, X. Dai, Z. Fang, and S. C. Zhang, Nat. Phys. 5, 438 (2009).
9 Z. Wang, Y. Sun, X.-Q. Chen, C. Franchini, G. Xu, H. Weng, X. Dai, and Z. Fang, Phys. Rev. B 85, 195320 (2012).
10 Z. Wang, H. Weng, Q. Wu, X. Dai, and Z. Fang, Phys. Rev. B 88, 125427 (2013).
11 X. Wan, A. M. Turner, A. Vishwanath, and S. Y. Savrasov, Phys. Rev. B 83, 205101 (2011).
12 G. Xu, H. Weng, Z. Wang, X. Dai, and Z. Fang, Phys. Rev. Lett. 107, 186806 (2011).
13 B. Q. Lv, H. M. Weng, B. B. Fu, X. P. Wang, H. Miao, J. Ma, P. Richard, X. C. Huang, L. X. Zhao, G. F. Chen, Z. Fang, X. Dai, T. Qian, and H. Ding, Phys. Rev. X 5, 031013 (2015).
14 S. Y. Xu, I. Belopolski, N. Alidoust, M. Neupane, G. Bian, C. Zhang, R. Sankar, G. Chang, Z. Yuan, and C. C. Lee, Science 349, 613 (2015).
15 H. Weng, Y. Liang, Q. Xu, R. Yu, Z. Fang, X. Dai, and Y. Kawazoe, Phys. Rev. B 92, 045108 (2015).
16 R. Yu, H. Weng, Z. Fang, X. Dai, and X. Hu, Phys. Rev. Lett. 115, 036807 (2015).
17 Y. Kim, B. J. Wieder, C. L. Kane, and A. M. Rappe, Phys. Rev. Lett. 115, 036806 (2015).
18 G. Bian, T.-R. Chang, R. Sankar, S.-Y. Xu, H. Zheng, T. Neupert, C.-K. Chiu, S.-M. Huang, G. Chang, I. Belopolski, D. S. Sanchez, M. Neupane, N. Alidoust, C. Liu, B. Wang, C.-C. Lee, H.-T. Jeng, C. Zhang, Z. Yuan, S. Jia, A. Bansil, F. Chou, H. Lin, and M. Z. Hasan, Nat. Commun. 7, 10556 (2016).
19 T. Bzdusek, Q. Wu, A. Ruegg, M. Sigrist, and A. A. Soluyanov, Nature 538, 75 (2016).
20 R. Li, H. Ma, X. Cheng, S. Wang, D. Li, Z. Zhang, Y. Li, and X.-Q. Chen, Phys. Rev. Lett. 117, 096401 (2016).
21 K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, Nature 438, 197 (2005).
22 A. K. Geim and K. S. Novoselov, Nat. Mater. 6, 183 (2007).
23 S. M. Young, S. Zaheer, J. C. Y. Teo, C. L. Kane, E. J. Mele, and A. M. Rappe, Phys. Rev. Lett. 108, 140405 (2012).
24 Q. D. Gibson, L. M. Schoop, L. Muechler, L. S. Xie, M. Hirschberger, N. P. Ong, R. Car, and R. J. Cava, Phys. Rev. B 91, 205128 (2015).
25 M. Z. Hasan and J. E. Moore, Ann. Rev. Condens. Matter Phys. 2, 55 (2011).
26 Z. K. Liu, J. Jiang, B. Zhou, Z. J. Wang, Y. Zhang, H. M. Weng, D. Prabhakaran, S. K. Mo, H. Peng, and P. Dedin, Nat. Mater. 13, 677 (2014).
27 M. Neupane, S.-Y. Xu, R. Sankar, N. Alidoust, G. Bian, C. Liu, I. Belopolski, T.-R. Chang, H.-T. Jeng, H. Lin, A. Bansil, F. Chou, and M. Z. Hasan, Nat. Commun. 5, 3786 (2014).
28 S. Borisenko, Q. Gibson, D. Evtushinsky, V. Zabolotnyy, B. B"uchner, and R. J. Cava, Phys. Rev. Lett. 113, 027603 (2014).
29 H. Y. Li, Z. Wang, C. Chen, Y. Shi, Y. Feng, A. Liang, Z. Xie, S. He, J. He, and Y. Peng, Sci. Rep. 4, 6106 (2013).
30 S. Jeon, B. B. Zhou, A. Gynis, B. E. Feldman, I. Kimchi, A. C. Potter, Q. D. Gibson, R. J. Cava, A. Vishwanath, and A. Yazdani, Nat. Mater. 13, 851 (2014).
31 Y. L. Chen, Z. K. Liu, B. Zhou, Y. Zhang, Z. J. Wang, H. M. Weng, D. Prabhakaran, S. K. Mo, Z. X. Shen, and Z. Fang, Science 343, 864 (2014).
32 S. Y. Xu, C. Liu, S. K. Kushwaha, R. Sankar, J. W. Krizan, I. Belopolski, M. Neupane, G. Bian, N. Alidoust, and T. R. Chang, Science 347, 294 (2015).
33 A. C. Potter, I. Kimchi, and A. Vishwanath, Nat. Commun. 5, 5161 (2014).
34 J. Xiong, S. K. Kushwaha, T. Liang, J. W. Krizan, M. Hirschberger, W. Wang, R. J. Cava, and N. P. Ong, Science 350, 413 (2015).
35 P. Goswami, J. H. Pixley, and S. Das Sarma, Phys. Rev. B 92, 075205 (2015).
36 S. A. Kulishch, M. E. Leonova, and L. G. Sevast‘Yanova, Zh. Otsch. Khim. 69, 681 (1999).
37 X. Cheng, R. Li, Y. Sun, X.-Q. Chen, D. Li, and Y. Li, Phys. Rev. B 89, 245201 (2014).
38 F. Guinea, M. I. Katsnelson, and A. K. Geim, Nat. Phys. 6, 30 (2009).
39 M. Bahramy, B.-J. Yang, R. Arita, and N. Nagaosa, Nat. Commun. 3, 679 (2012).
40 J. Ruan, S.-K. Jian, H. Yao, H. Zhang, S.-C. Zhang, and D. Xing, Nat. Commun. 7, 11136 (2016).
41 S. Zhang, Q. Wu, L. Schoop, M. N. Ali, Y. Shi, N. Ni, Q. Gibson, S. Jiang, V. Sidorov, W. Yi, J. Guo, Y. Zhou, D. Wu, P. Gao, D. Gu, C. Zhang, S. Jiang, K. Yang, A. Li, Y. Li, X. Li, J. Liu, X. Dai, Z. Fang, R. J. Cava, L. Sun, and Z. Zhao, Phys. Rev. B 91, 165133 (2015).
42 L. He, Y. Jia, S. Zhang, X. Hong, C. Jin, and S. Li, npj Quantum. Mater. 1, 16004 (2016).
43 H. Wang, H. Wang, H. Liu, H. Lu, W. Yang, S. Jia, X.-J. Liu, X. Xie, J. Wei, and J. Wang, Nat. mater. 15, 38 (2016).
44 Y. Zhou, P. Lu, Y. Du, X. Zhu, G. Zhang, R. Zhang, D. Shao, X. Chen, X. Wang, M. Tian, J. Sun, X. Wan, Z. Yang, W. Yang, Y. Zhang, and D. Xing, Phys. Rev. Lett. 117, 146402 (2016).
Y. Zhou, J. Wu, W. Ning, N. Li, Y. Du, X. Chen, R. Zhang, Z. Chi, X. Wang, X. Zhu, P. Lu, C. Ji, X. Wan, Z. Yang, J. Sun, W. Yang, M. Tian, Y. Zhang, and H.-k. Mao, Proc. Natl. Acad. of Sci. USA **113**, 2904 (2016).

P. Lu, J.-S. Kim, J. Yang, H. Gao, J. Wu, D. Shao, B. Li, D. Zhou, J. Sun, D. Akinwande, D. Xing, and J.-F. Lin, Phys. Rev. B **94**, 224512 (2016).

X. Chen, P. Lu, X. Wang, Y. Zhou, C. An, Y. Zhou, C. Xian, H. Gao, Z. Guo, C. Park, B. Hou, K. Peng, X. Zhou, Y. Xiong, J. Sun, Z. Yang, D. Xing, and Y. Zhang, ArXiv e-prints (2016), arXiv:1608.06763.

Y. Li, Y. Zhou, Z. Guo, X. Chen, P. Lu, X. Wang, C. An, Y. Zhou, J. Xing, G. Du, X. Zhu, H. Yang, J. Sun, Z. Yang, Y. Zhang, and H.-H. Wen, arXiv preprint arXiv:1611.02548 (2016).

X. Cheng, R. Li, D. Li, Y. Li, and X.-Q. Chen, Phys. Chem. Chem. Phys. **17**, 6933 (2015).

X. Cheng, R. Li, D. Li, Y. Li, and X.-Q. Chen, Phys. Rev. B **92**, 155109 (2015).

M. E. Leonova, S. A. Kulinich, and L. G. Sevast’yanova, Exp. Geosci. **7**, 55 (1998).

M. E. Leonova, I. K. Bdikin, S. A. Kulinich, O. K. Gulish, L. G. Sevast’Yanova, and K. P. Burdina, Inorg. Mater. **39**, 266 (2003).

J. M. Luttinger, Phys. Rev. **102**, 1030 (1956).

C. J. Pickard and R. J. Needs, Phys. Rev. Lett. **97**, 045504 (2006).

C. J. Pickard and R. J. Needs, J. Phys.: Conden. Matter **23**, 053201 (2011).

G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

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

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

P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k: An Augmented Plane Wave plus Local Orbitals Program for Calculating Crystal Properties (Karlheinz Schwarz, Technische Universitaet Wien, Vienna, 2001).

L. Fu and C. L. Kane, Phys. Rev. B **76**, 045302 (2007).

N. Marzari and D. Vanderbilt, Phys. Rev. B **56**, 12847 (1997).

I. Souza, N. Marzari, and D. Vanderbilt, Phys. Rev. B **65**, 035109 (2001).

N. Marzari, A. A. Mostofi, J. R. Yates, I. Souza, and D. Vanderbilt, Rev. Mod. Phys. **84**, 1419 (2012).