RESEARCH ARTICLE | AUGUST 29 2023

Coexistence of quantum spin Hall and magnetic states in zigzag bismuth nanoribbons FREE

Special Collection: Accelerate Materials Discovery and Phenomena

Ivan I. Naumov ; Pratibha Dev

Appl. Phys. Lett. 123, 093104 (2023)
https://doi.org/10.1063/5.0160159

Applied Physics Letters ARTICLE pubs.aip.org/aip/apl

Coexistence of quantum spin Hall and magnetic states in zigzag bismuth nanoribbons

Cite as: Appl. Phys. Lett. **123**, 093104 (2023); doi: 10.1063/5.0160159
Submitted: 30 May 2023 · Accepted: 18 August 2023 ·
Published Online: 29 August 2023

Ivan I. Naumov and Pratibha Dev[a)]

AFFILIATIONS

Department of Physics and Astronomy, Howard University, 2355 6th Street, NW, Washington, DC 20059, USA

Note: This paper is part of the APL Special Collection on Accelerate Materials Discovery and Phenomena.
[a)]**Author to whom correspondence should be addressed:** pratibha.dev@howard.edu

ABSTRACT

Chemical modifications and/or simple vertical stacking of disparate van der Waals layered crystals can be used as a materials design approach for creating novel phases of matter. Here, using *ab initio* computations, we demonstrate the realization of an unusual state in a bismuth nanoribbon decorated with nitrogen atoms along one of the edges. In this phase, the quantum spin Hall state on one edge of the nanoribbon coexists with the ferromagnetism on the other edge. Such a coexistence is made possible by the short-range nature of the exchange interactions on the magnetic edge. As a result, the quantum spin Hall state on the opposite edge of the nanoribbon does not feel the local breaking of time-reversal symmetry on the magnetic edge. While the edge with quantum spin Hall state exhibits the typical spin-helical texture associated with the state, the magnetic edge displays $\pm\boldsymbol{k}$-asymmetry due to the interplay of Rashba and exchange effects. The latter is also a half-metal and can generate a fully spin-polarized current. We demonstrate that this coexistence of states is robust and that it is exhibited even when the nitrogen-decorated nanoribbon is placed on a substrate. In addition, with a proof-of-principle heterostructure, composed of an undecorated bismuth nanoribbon on hexagonal boron nitride, we show that this mixture of states can potentially exist even without passivation with nitrogen-atoms. In the heterostructure, an unequal relaxation along the two edges of the nanoribbon is found to be responsible for the coexistence of two states.

Bismuth (Bi) (111) bilayer, a graphene-like material with buckled honeycomb lattice, is a two-dimensional topological insulator exhibiting the quantum spin Hall effect (QSHE). The edges of nanoribbons (NRs) created from Bi bilayers form true one-dimensional (1D) Rashba systems, which display gapless helical edge states.[1–10] A free-standing bismuth NR that has been allowed to fully relax is nonmagnetic due to the reconstruction at the edges, which leads to the pairing of electrons in the dangling bonds along the edges.[8–10] However, this relaxation can be constrained by a number of means, such as by placing the NR on an appropriate substrate or by decorating the edges with nitrogen atoms.[10] In such cases, Bi NRs can also have stable magnetic solutions, corresponding to the antiferromagnetic (AFM) and ferromagnetic (FM) spin orientations between the edges.[10] The magnetic states are physically interesting in their own right, demonstrating an interplay between Rashba and exchange effects that occurs locally, that is, independently at each edge. This locality is due to the involvement of topological edge states and the short-range character of exchange interactions.

Here, we show the fundamental possibility of a different situation, wherein the QSHE state on one edge of the Bi NR can coexist with the FM state on the other edge. This unusual solution is possible because of the aforementioned locality of the Rashba and exchange effects. As a consequence, even though, strictly speaking, the time-reversal symmetry in the system is broken, locally it does not prevent the realization of the QSHE state on one edge while the other edge is magnetic. We demonstrate that such a "mixed" phase, in which the QSHE coexists with the magnetic state within the same system, can be realized by decorating one of the edges of the zigzag NR with nitrogen (N) atoms, leaving the other edge undecorated. By placing this decorated NR on hBN, we further demonstrate that this system retains its mixed phase even in the presence of a substrate, showing the robustness of this new phase. Finally, we argue that the substrate itself can induce a mixed phase without the presence of nitrogen. This is due to the buckled nature of the Bi-bilayer, which leads to asymmetric relaxation of the two opposite edges, resulting in the mixed phase.

In order to demonstrate that a single system can host these two seemingly mutually exclusive states, we performed *ab initio* calculations for Bi zigzag nanoribbons, which were decorated with N atoms and/or placed on a hexagonal boron nitride (hBN) monolayer as a substrate. The Vienna ab-initio simulation package (VASP)[11,12] was

employed in our calculations, which used the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE)[13] to describe the exchange-correlation potential. The projected augmented wave (PAW) method[14] was used to describe the interaction between the ionic cores and electrons. All of the structures studied here were relaxed until the difference in total energies between two ionic steps became smaller than 1×10^{-4} eV. The kinetic energy cutoff was set to 400 eV. A $48 \times 1 \times 1$ Monkhorst–Pack $\boldsymbol{k}$-point grid was used for the Brillouin zone sampling. The orientation of the zigzag Bi(111) nanoribbons was chosen such that they were of infinite length in the x-direction and of finite width in the y-direction. As periodic boundary conditions were used, we added a vacuum gap of 25 Å in both the y- and z-directions to ensure negligible wavefunction overlap between the images. Each of the under-coordinated Bi atoms along one of the edges of the Bi NR was passivated with a N atom, resulting in the so-called Klein (or "bearded") edge structure as seen in Fig. 1(a). The supercell for this decorated freestanding Bi NR consisted of 32 Bi atoms and 1 N atom. In order to study the robustness of the mixed phase, we created a heterostructure by placing nitrogen-decorated Bi NR on an hBN monolayer. This vertical heterostructure can be described as a (1×1) Bi bilayer on $(\sqrt{3} \times \sqrt{3})$ hBN with a very small lattice mismatch of an only about 0.2%–0.3%. This Moiré supercell used in our work contained 24 atoms in the Bi NR, 1 N atom passivating one of the NR edges and a total of 96-atoms in the hBN layer. Although initially commensurate, in the process of relaxation the simulated heterostructure N-Bi/hBN became incommensurate in the y-direction (i.e., along the direction of the NR's finite width), while the commensurability along the infinite x-direction was retained. For the Bi NRs passivated with nitrogen (whether freestanding or on hBN substrate), all calculations (including atomic relaxation) incorporated spin–orbit coupling (SOC) by employing fully relativistic pseudopotentials.

We begin with the freestanding Bi zigzag NR in which one of the edges is passivated with nitrogen atoms. Upon relaxation, we find that Bi and N atoms form a strong covalent bond, with a bond length of 2.16 Å. The self-consistent calculation yielded a solution with a ferromagnetic (FM) spin alignment along the N-decorated edge, with a net magnetic moment of (0.00, −1.14, and 1.49) μ_B per supercell, and a quantum spin Hall state on the opposite edge. The magnetic moment is mostly contributed by the nitrogen's p_y- and p_z-derived states. The distribution of magnetization along the (dominant) z-direction is plotted in Figs. 1(b) and 1(c), which are the side and top views of the nanoribbon. From the spin density plots of Figs. 1(b) and 1(c), it is evident that the N atoms carry most of the magnetic moment in the supercell. Although the Bi atoms those are adjacent to the N atoms also contribute to the magnetic moment, this contribution decreases rapidly in magnitude, oscillating in the direction when moving toward the center of the NRs.

The band structure of the freestanding, decorated Bi NR is presented in Fig. 2(a), showing the spin-split magnetic bands close to the Fermi level, along with the characteristic topological bands those are degenerated at the time-reversal invariant momenta (TRIM) points (±X-points). In order to further understand the origin of these bands, we also plot the spin-resolved band structure, showing the dominant $\pm S_z$ spin projection in Fig. 2(b) and further plot its atom-resolved variants in Figs. 2(c) and 2(d). In particular, Fig. 2(c), which plots the band structure projected onto the N atoms, confirms that it is the N atoms those are primarily responsible for the magnetism. This "magnetic" band structure is spin polarized, with an exchange gap of about 1.5 eV at the –X and X points, indicating that the QSHE is destroyed on the edge decorated with nitrogen. Moreover, a careful inspection of Fig. 2(c) reveals that these bands are asymmetric relative to the origin ($\boldsymbol{k} = 0$). This asymmetry is due to the combined effects of Rashba SOC and FM ordering.[10] Figure 2(d) plots the band structure projected onto the two outermost Bi atoms on the opposite (undecorated) edge. This band structure displays the expected topological QSHE states, which are similar to the topological states reported for free-standing nanoribbons.[1–4,7,8,10] These topological bands span the bulk bandgap, connecting the valence and conduction bands as expected from the topological surface/edge states, and are degenerated at the ±X-points. The QSHE states are characterized by a helical spin texture as can be seen from the spin-resolved band structure in Fig. 2(d). Thus, we see that in this 1D system, the QSHE state and magnetic ordering are observed simultaneously. This is due to the fact that the Rashba effect and the exchange effect act locally on each edge.

In order to explore the effects a substrate can have on the mixed state, we placed the N-decorated Bi NR on an hBN monolayer to create a N-Bi/hBN heterostructure. Although there are infinite possibilities corresponding to the horizontal shifts of the Bi-bilayer relative to the hBN monolayer, they all lead to similar results. Therefore, we consider only one starting alignment (i.e., stacking orders before relaxation) between the two components—Bi and hBN—of the composite. In the chosen N-Bi/hBN structure, all Bi-atoms of the bilayer sit directly on top of the B-atoms in hBN. As seen in Figs. 3(a)–3(d), in the presence of the substrate, the band structure retains its most

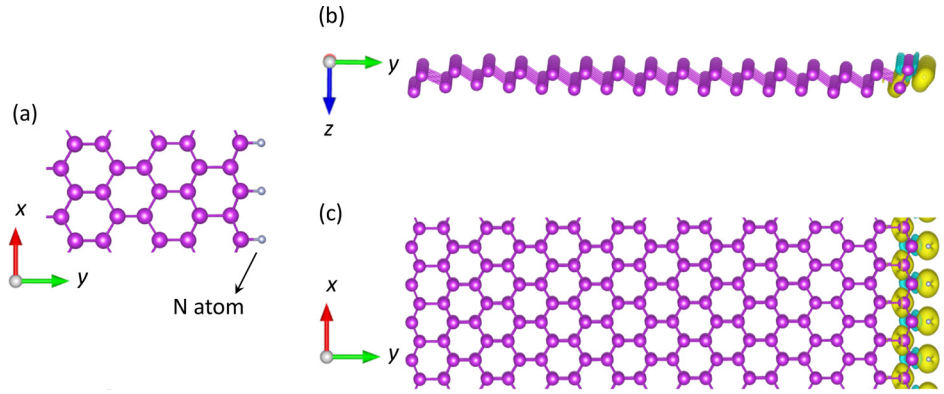

FIG. 1. Zigzag Bi NR decorated with nitrogen (N) atoms along one of the edges. (a) Klein (bearded) structure of N-decorated edge. (b) Side and (c) top views of spin-density isosurface plot, showing the dominant z-component. Blue (yellow) color indicates the negative (positive) isovalues in the isosurface plot. The total magnetic moment of the system is (0.00, –1.14, and 1.49) μ_B.

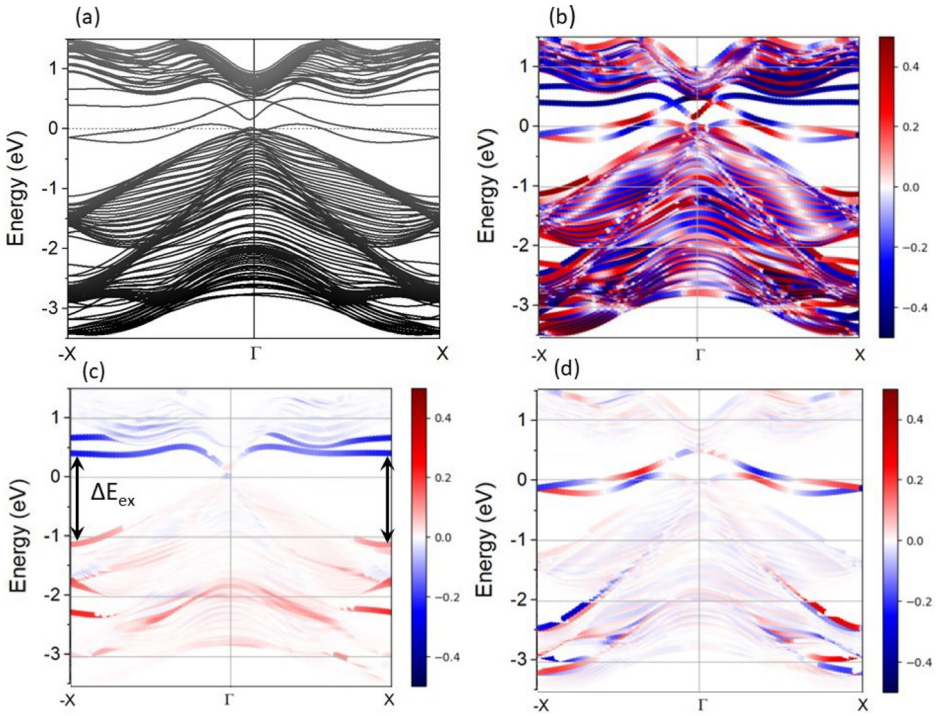

FIG. 2. Electronic structure of the mixed-phase of a Bi zigzag NR decorated with nitrogen (along one edge). (a) Band structure, showing both the topological states and states with exchange splitting around the Fermi level. (b) Spin-projected band structure, taking into account contributions from all atoms. Only $\pm S_z$ spin projection is chosen because the *z*-component of the net magnetic moment is dominant. (c) Spin-projected band structure showing only the contributions from the edge N atoms to the dominant $\pm S_z$ spin projection. The double arrows indicate the exchange gaps at the –X and X points. (d) Contribution of two outermost Bi atoms along the undecorated edge to the spin-projected band structure (for $\pm S_z$). The band structure with $\pm S_y$ spin projections is similar to that with $\pm S_z$ projections in many respects (not shown), whereas the expectation values of $\pm S_x$ are negligibly small (not shown).

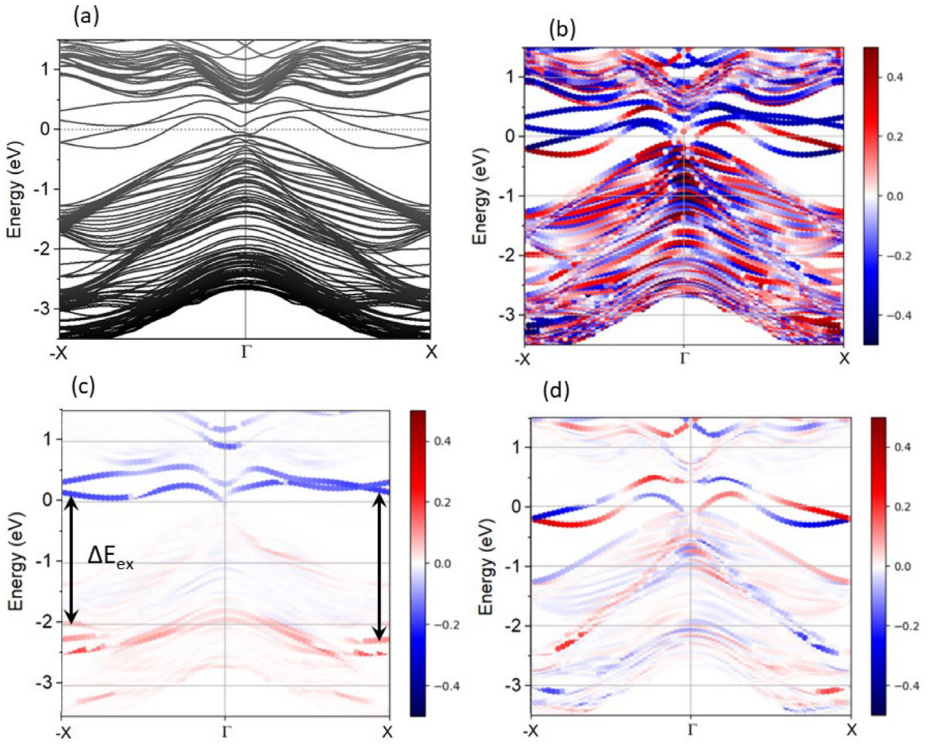

FIG. 3. Electronic structure of the mixed-phase in the N-Bi/hBN heterostructure. (a) Band structure, showing both the topological states and states with exchange splitting around Fermi level. (b) Spin-projected band structure, taking into account contributions from all atoms. Only $\pm S_y$ spin projection is chosen because the *y*-component of the net magnetic moment becomes dominant once N-decorated Bi is placed on hBN. (c) Spin-projected band structure showing only the contributions from the N atom to the dominant $\pm S_y$ spin projection. The double arrows indicate the exchange gaps at the –X and X points. (d) Contribution of two outermost Bi atoms along the undecorated edge to the spin-projected band structure (for $\pm S_y$).

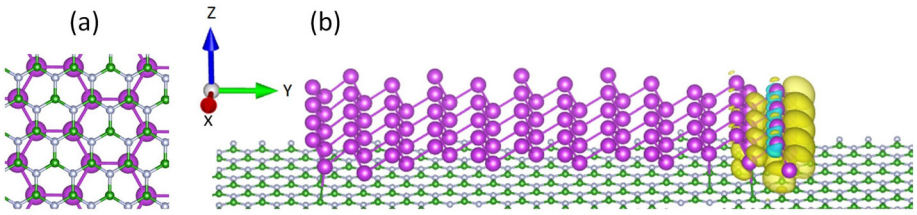

FIG. 4. Undecorated Bi/hBN heterostructure. (a) Top-view of the proof-of-principle Bi/hBN heterostructure. The magenta, gray, and green spheres are Bi, N, and B atoms, respectively. Note that the Bi bilayer and hBN monolayer are incommensurate in the *y*-direction (i.e., along the direction of the NR's finite-width), while commensurate along the infinite *x*-direction. (b) Spin density plot for the Bi/hBN, showing the dominant *z*-component (corresponding to FM solutions) blue (yellow) color indicates the negative (positive) isovalues in the isosurface plot. The total magnetic moment of the Bi/hBN heterosructures is (0.00, −0.25, and 0.29) μ_B.

important features around the Fermi level. This is due to the fact that the hBN monolayer is a wide bandgap semiconductor, with its states energetically well-separated from the Bi nanoribbon-derived states around the Fermi level. Hence, we find that the system still exhibits a "mixed state," with some modifications. In particular, the net magnetic moment is now (0.82, 1.35, 0.87)μ_B. Though its absolute value decreases only slightly from 1.87 μ_B to 1.80 μ_B, it rotates in such a way that its *x*-component becomes nonzero, while its *y*-component becomes dominant.

In addition to using chemical modifications (such as, the nitrogen-atom decoration) for creating the mixed phase, one can envision that this phase can also be realized by stacking of the Bi NR on an appropriate substrate. Within such a heterostructure, one edge of the NR that terminates in the lower Bi atoms (within the buckled Bi-bilayer) is closer to the substrate as compared to the other edge that terminates in the upper Bi atoms of the buckled Bi-bilayer. In this case, different substrate effects that inhibit relaxation, such as substrate friction,[15–17] affect the two edges differently, resulting in asymmetrical relaxation of the two edges. A mixed state can then result if the edge closer to the substrate is prevented from undergoing significant deviation from its "ideal" (i.e., as-created) structure, making it magnetic, while the opposite edge, being farther from the substrate, can undergo considerable relaxation, resulting in the QSHE state that is seen in fully relaxed freestanding NRs. To study this possibility, we placed an undecorated zigzag Bi NR on a monolayer of hBN, creating a Bi/hBN heterostructure. The starting vertical alignment (before relaxation) was chosen such that it places the Bi atoms directly above the B atoms in hBN, as shown in Fig. 4(a). We find that for the Bi/hBN structure to develop magnetism, it has to be strained. In what follows, we present our results for a structure that was stretched along the infinite direction (i.e., *x*-direction) by about 4.0%. Also, the inclusion of the SOC during relaxation reduces the magnetic moment. Since the substrate effects are subtler as compared to the use of chemical modification to create the mixed state, SOC was not included during the relaxation process; however, it was taken into account when determining the electronic structure properties of the optimized heterostructure. Here, it should be pointed out that hBN is just one of many possible substrates and Bi NR is one of many 1D structures that can be created from other layered topological materials. Hence, it is very likely that the requirements (such as, applying strain) for observing a mixed state are artificial and can be eliminated for other substrates and/or 1D systems (i.e., NRs made from layered materials other than bismuth). Figure 4(b) presents the spin density for the heterostructure, showing a magnetic right edge with a total magnetic moment of (0.00, −0.24, and 0.29) μ_B. The outermost Bi atoms on the right edge carry most of this magnetic moment. In the hBN-substrate, only the nitrogen atoms closest to the magnetic edges are magnetized, with the magnetization in the same direction as the outermost Bi atoms on the right edge. As expected, the atomic relaxation is more pronounced near the left edge, where the Bi atoms are further away from hBN. The edge-resolved band structure of the Bi/hBN system is presented in Fig. 5(a), which shows the bands localized at the left edge in green and on the right edge in orange. The former are similar to the QSHE states shown in Figs. 2 and 3. On the other hand, the bands localized on the right edge (shown in orange) resemble those reported for the magnetic solutions in an earlier work.[10] The spin-resolved band structure plots in Figs. 5(b) and 5(c) show the helical spin texture of the QSHE states.

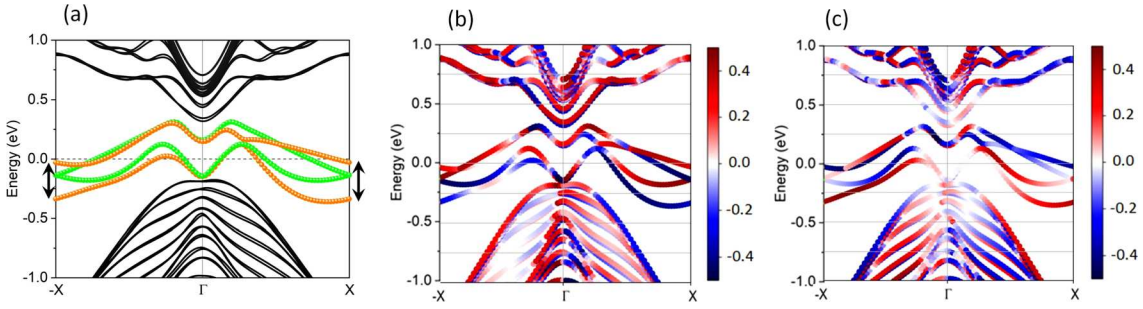

FIG. 5. Band structure for the Bi/hBN heterostructure with the FM configuration, without (a) and with (b) and (c) spin projections. In subfigure (a), the edge bands localized on the left and right edges of the nanoribbons are indicated by green and orange colors, respectively. The two double arrows indicate the exchange energy gaps at the –X and X points on the magnetic edge. The panels (b) and (c) correspond to the $\pm S_y$ and $\pm S_z$ spin projections, respectively.

To further explore the role played by the substrate, we removed the hBN layer, while freezing the geometry of the undecorated Bi NR to its equilibrium geometry within the heterostructure. We find that the Bi NR with its distorted geometry (due to inequivalent relaxation at the edges) retains its one-edged magnetic ordering. Moreover, in going to the freestanding (albeit distorted) Bi-nanoribbon, the total magnetic moment increases slightly to a value of (0.00, −0.30, and 0.33) μ_B. Hence, we find that in our proof-of-principle heterostructure (Bi/hBN), the substrate plays two roles: (i) it reduces the extent to which the edge closer to the hBN layer relaxes, facilitating the magnetic ordering, and (ii) it lowers the total magnetic moment relative to that which would exist in the freestanding NR alone. This is due to charge transfer between the two subsystems within the heterostructure, which results in the partial saturation of dangling bonds, reducing the net magnetic moment.

We also find that by simple in-plane interlayer sliding, the proof-of-principle heterostructure Bi/hBN can be transformed into another one, where the Bi atoms mostly sit on top of the N atoms, but not B atoms. Such a sliding is quite possible because our system belongs to a class of van der Waals materials where the sliding energy barriers are relatively low. This modified Bi/hBN heterostructure develops magnetic moments on both edges, with a FM ordering between the edges. As a result, the magnitude of the magnetic moment increases two and a half times. If in-plane sliding can be implemented, it would represent a new and unusual way of changing of the edge states. In particular, it could serve as a switching mode between the mixed QSHE-magnetic state and the purely magnetic state.

Finally, Figs. 2 and 3 show that if the Fermi level is tuned (by gating) so that it is increased by about 0.3 eV, the magnetic edge of the N-decorated Bi NRs will behave as a half-metal. The same half-metallicity is realized in the undecorated ribbons placed on an hBN monolayer, already at the Fermi level (Fig. 5). In all these cases, electrical current at magnetic edges can be completely spin polarized (mostly perpendicular to their infinite direction), in both flow directions. At the same time, on the opposite, "quantum spin Hall" edge, the electric current can be spin filtered in the sense that the up spins propagate in one direction, while the down spins propagate in the opposite direction. We believe that Bi NRs, which have both half-metallic and "helical" states, can find application in spin electronics.

In summary, we show that an unexpected state can be obtained in Bi NRs decorated with nitrogen or placed on an hBN monolayer as a prototype substrate. In this state, the quantum-spin Hall state at one edge of the Bi NR coexists with the ferromagnetic order at the other edge of the NR. The topological edge state exhibits typical spin-helical texture, while the magnetic (half-metallic) state localized to the other edge exhibits the typical $\pm\boldsymbol{k}$-asymmetry due to interplay of Rashba and exchange effects. There are two factors those make the existence of such a mixed state possible. The first factor that plays a role in realizing the mixed state is the structural asymmetry between the edges. This itself is caused by chemical modification of one edge or by the fact that the substrate interacts differently with the opposite edges of the NR, and as a result, the degree of relaxation of the opposite edges also becomes different. The second important factor is that the short-range nature of the exchange interaction and the significant localization of the topological edge states virtually suppresses any proximity effects between edges. We believe that the coexistence of what seems to be mutually exclusive phenomena in the mixed state solution may also exist in other one-dimensional systems, for which the Bi NR can serve as a prototype. Our study also suggests that one can transition between the three possible states—purely non-magnetic (quantum spin Hall) state, purely magnetic state, and the mixed state—of the Bi NR by in-plane interlayer sliding of the NR on a substrate. This work is not only a scientific curiosity that explores a mixed phase that is made possible by chemical modifications or by stacking disparate van der Waals materials, but it may also open a new avenue for spintronics applications.

This work was supported by the W. M. Keck Foundation and the NSF Grant No. DMR-1752840. This work used the Expanse cluster at SDSC through allocation PHY180014 from the Advanced Cyberinfrastructure Coordination Ecosystem: Services & Support (ACCESS) program, which is supported by National Science Foundation Grants Nos. 2138259, 2138286, 2138307, 2137603, and 2138296, and the Maryland Advanced Research Computing Center. We also acknowledge VESTA 3 software for three-dimensional visualization of crystals and volumetric data and the use of *PyProcar* to create figures with spin textures.[18]

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Ivan I. Naumov: Writing – review & editing (equal). **Pratibha Dev:** Writing – review & editing (equal).

Data Availability

The data that support the findings of this study are available within the article.

REFERENCES

[1]S. Murakami, "Quantum spin Hall effect and enhanced magnetic response by spin-orbit coupling," Phys. Rev. Lett. **97**, 236805 (2006).
[2]F. Yang, L. Miao, Z. F. Wang, M.-Y. Yao, F. Zhu, Y. R. Song, M.-X. Wang, J.-P. Xu, A. V. Fedorov, Z. Sun, G. B. Zhang, C. Liu, F. Liu, D. Qian, C. L. Gao, and J.-F. Jia, "Spatial and energy distribution of topological edge states in single Bi(111) bilayer," Phys. Rev. Lett. **109**, 016801 (2012).
[3]H. Kotaka, F. Ishii, M. Saito, T. Nagao, and S. Yaginuma, "Edge states of Bi nanoribbons on Bi substrates: First-principles density functional study," Jpn. J. Appl. Phys., Part 1 **51**, 025201 (2012).
[4]D. Wang, L. Chen, H. Liu, and X. Wang, "Electronic structures and topological properties of Bi(111) ultrathin films," J. Phys. Soc. Jpn. **82**, 094712 (2013).
[5]Z. F. Wang, L. Chen, and F. Liu, "Tuning topological edge states of Bi(111) bilayer film by edge adsorption," Nano Lett. **14**, 2879 (2014).
[6]X. Li, H. Liu, H. Jiang, F. Wang, and J. Feng, "Edge engineering of a topological Bi(111) bilayer," Phys. Rev. B **90**, 165412 (2014).
[7]H. W. Yeom, K.-H. Jin, and S.-H. Jhi, "Topological fate of edge states of Bi single bilayer on Bi(111)," Phys. Rev. B **93**, 075435 (2016).
[8]S.-M. Jeong, S. Yi, H.-J. Kim, G. Bihlmayer, and J.-H. Cho, "Competing edge structures of Sb and Bi bilayers generated by trivial and nontrivial band topologies," Phys. Rev. B **98**, 075402 (2018).
[9]L. Peng, J.-J. Xian, P. Tang, A. Rubio, S.-C. Zhang, W. Zhang, and Y.-S. Fu, "Visualizing topological edge states of single and double bilayer Bi supported, on multibilayer Bi(111) films," Phys. Rev. B **98**, 245108 (2018).

[10]I. I. Naumov and P. Dev, "One-dimensional magnetism and Rashba-like effects in zigzag bismuth nanoribbons," Phys. Rev. Mater. **7**, 026204 (2023).
[11]G. Kresse and D. Joubert, "From ultrasoft pseudopotentials to the projector augmented-wave method," Phys. Rev. B **59**, 1758 (1999).
[12]G. Kresse and J. Furthmüller, "Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set," Phys. Rev. B **54**, 11169 (1996).
[13]J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized gradient approximation made simple," Phys. Rev. Lett. **77**, 3865 (1996).
[14]P. E. Blöchl, "Projector augmented-wave method," Phys. Rev. B **50**, 17953 (1994).
[15]P. Manchanda, P. Kumar, and P. Dev, "Thickness dependence of hydrogen-induced phase transition in $MoTe_2$," Phys. Rev. B **101**, 144104 (2020).
[16]P. Manchanda, P. Kumar, and P. Dev, "Defect-induced 4p-magnetism in layered platinum diselenide," Phys. Rev. B **103**, 144403 (2021).
[17]S. K. Narayanan and P. Dev, "Substrate-induced modulation of quantum emitter properties in 2D hexagonal boron nitride: Implications for defect-based single photon sources in 2D Layers," ACS Appl. Nano Mater. **6**, 3446 (2023).
[18]U. Herath, P. Tavadze, X. He, E. Bousquet, S. Singh, F. Muñoz, and A. H. Romero, "PyProcar: A Python library for electronic structure pre/post-processing," Comput. Phys. Commun. **251**, 107080 (2020).