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PHYSICS

Natural van der Waals heterostructural single crystals with both magnetic and topological properties

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Heterostructures having both magnetism and topology are promising materials for the realization of exotic topological quantum states while challenging in synthesis and engineering. Here, we report natural magnetic van der Waals heterostructures of $(\text{MnBi}_2\text{Te}_4)_m(\text{Bi}_2\text{Te}_3)_n$ that exhibit controllable magnetic properties while maintaining their topological surface states. The interlayer antiferromagnetic exchange coupling is gradually weakened as the separation of magnetic layers increases, and an anomalous Hall effect that is well coupled with magnetization and shows ferromagnetic hysteresis was observed below 5 K. The obtained homogeneous heterostructure with atomically sharp interface and intrinsic magnetic properties will be an ideal platform for studying the quantum anomalous Hall effect, axion insulator states, and the topological magnetoelectric effect.

INTRODUCTION

Magnetic heterostructures have attracted considerable attention in the field of condensed matter physics for new spintronics and emerging topotronics (1–15). Research interest in magnetic heterostructures increased with the emergence of spintronics in the 1980s (1–2). Well-established deposition techniques for thin film growth, such as molecular beam epitaxy, pulsed laser deposition, and sputtering have given rise to the fast growth of this field, where unique properties such as giant magnetoresistance, initially observed in (001)Fe/(001)Cr superlattices (4), and tunneling magnetoresistance have been shown to be core technologies for digital information storage (1). However, the fabrication of magnetic heterostructures has long been limited by deposition techniques, hindering wide studies of the unique materials systems. Although the transfer method has recently been frequently used to prepare van der Waals heterostructures, it also requires sophisticated techniques with care (16).

Recently, heterostructures combined with magnetic layers and topological insulator (TI) layers have led to a rising field for the realization of exotic topological quantum states, including the quantum anomalous Hall effect (QAHE), axion insulator states, and the topological magnetoelectric effect (5–15). However, a homogeneous heterostructure with atomically sharp interface and intrinsic magnetic properties, believed to be an ideal platform for studying such topological quantum effects, is still experimentally elusive.

In the present work, we report the naturally occurring van der Waals heterostructures of $(\text{MnBi}_2\text{Te}_4)_m(\text{Bi}_2\text{Te}_3)_n$, which show controllable magnetic properties and topological surface states (SSs). Single crystals can be prepared using flux method. MnBi_4Te_7 ($m = n = 1$) and $\text{MnBi}_6\text{Te}_{10}$ ($m = 1$ and $n = 2$) are identified by x-ray dif-

fraction (XRD) measurements, and the heterogeneous structures are observed directly using a scanning transmission electron microscope (STEM). As the interlayer antiferromagnetic (AFM) exchange interactions are gradually weakened by increasing the separation of magnetic layers, the present materials turn into a magnetic order competing system and a ferromagnetic (FM) state could be stabilized below 5 K. As the magnetization has an out-of-plane easy axis, an anomalous Hall (AH) effect that is well coupled with magnetization is observed. The nontrivial electronic structures of MnBi_4Te_7 , both bulk and surface, are investigated using density functional theory (DFT) calculations, and the present compound is proved to be an AFM TI. The SSs are detected experimentally by angle-resolved photoemission spectroscopy (ARPES) measurements, showing a gap (120 meV at 20 K) due to the breakdown of time reversal symmetry. Therefore, the present materials system will provide a platform for investigating various interests in spintronics and topotronics, including spin valve states, QAHE, axion insulator states, two-dimensional van der Waals magnets, etc.

RESULTS

MnBi_2Te_4 was recently reported to be the first intrinsic van der Waals antiferromagnet showing topological nontrivial SS (10–13). It shares a similar crystal structure with Bi_2Te_3 , a typical TI. Along the c axis, Bi_2Te_3 is composed of Te-Bi-Te-Bi-Te quintuple atomic layers (QLs) held together by van der Waals forces, while MnBi_2Te_4 is composed of Te-Bi-Te-Mn-Te-Bi-Te septuple atomic layers (SLs), where each layer is equal to a QL intercalated by a MnTe layer (Fig. 1, A, B, E, and F, and fig. S1, A and B). As the two van der Waals materials have similar lattice constants in the a - b plane (the lattice mismatch is only around 1.3%), it would be interesting to check the possibility of synthesizing a natural heterostructure with alternating QL and SL following a new periodicity along the c axis (17).

Following this assumption, we prepared polycrystalline samples of $(\text{MnBi}_2\text{Te}_4)_m(\text{Bi}_2\text{Te}_3)_n$ using a solid-state reaction route, and their crystal structures are shown in fig. S1 and table S1. MnBi_4Te_7 ($m = n = 1$) and $\text{MnBi}_6\text{Te}_{10}$ ($m = 1$ and $n = 2$) are identified as natural van der Waals heterostructures (fig. S1F) in which SLs are separated by one or two QLs, respectively, as spacers (Fig. 1, C and D). As with Bi_2Te_3 and MnBi_2Te_4 , $\text{MnBi}_6\text{Te}_{10}$ adopts a trigonal structure with a space group of $R\bar{3}m$, while MnBi_4Te_7 adopts a space group of $P\bar{3}m1$.

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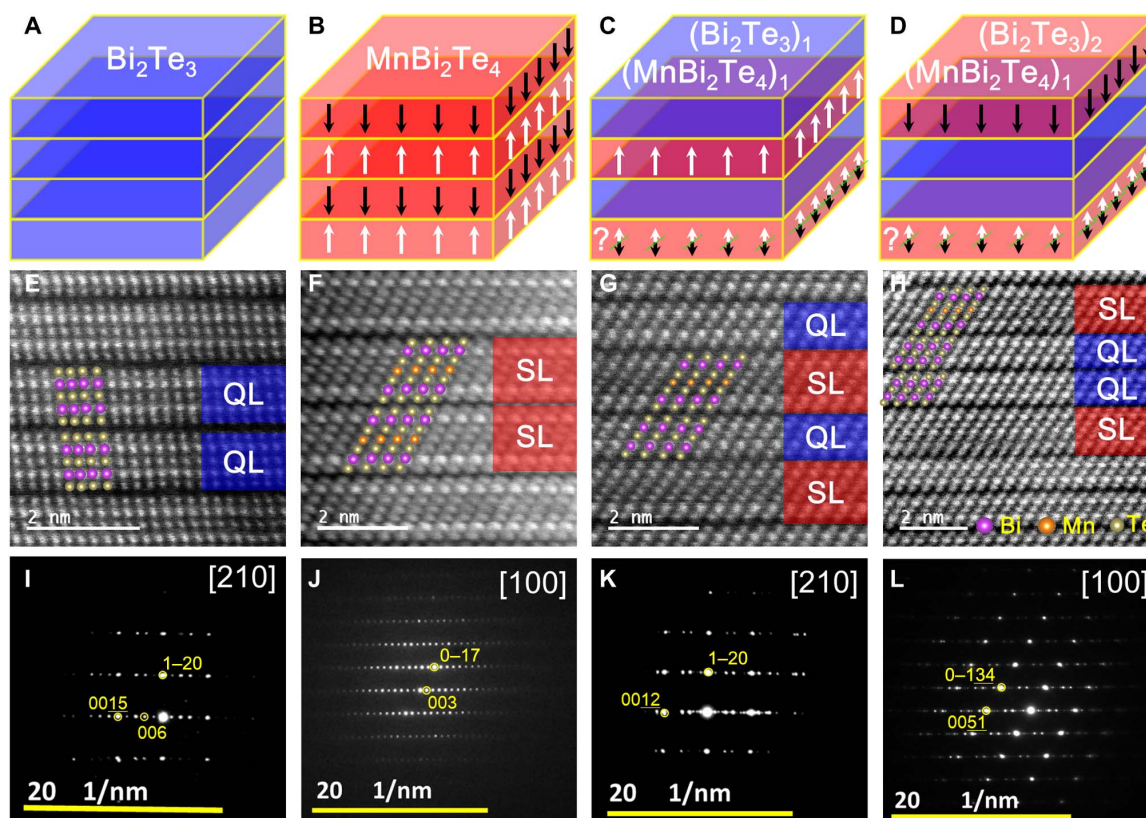


Fig. 1. Magnetic van der Waals heterostructures of $(\text{MnBi}_2\text{Te}_4)_m(\text{Bi}_2\text{Te}_3)_n$. (A to D) Schematics of the evolution of the heterostructures. The arrows show the spin orientation of Mn with black pointing down and white pointing up. The question marks in (C) and (D) show the uncertainty of the spin orientations due to complex magnetic interactions. (E to H) Atomic resolution high-angle annular dark-field (HAADF)-STEM images of the compounds displayed in (A) to (D). The images are taken along a zone axis perpendicular to the *c* axis. QL stands for quintuple layer and SL stands for septuple layer. (I to L) Selected-area electron diffraction (SAED) patterns of the compounds shown in (A) to (D).

The direct evidence of heterostructures is obtained by high-angle annular dark-field (HAADF)-STEM measurements (for polycrystalline samples), as shown in Fig. 1, E to H and fig. S2. The atomic resolution images are highly consistent with crystal structures obtained through XRD measurements and the proposed model (Fig. 1, A to D), showing QL and SL as well as van der Waals gaps. The high degree of crystallinity of the prepared samples can also be confirmed by the selected-area electron diffraction (SAED) patterns (Fig. 1, I to L) and the fast Fourier transform patterns of the obtained HAADF-STEM images (fig. S2). The distinct SAED patterns are mainly the results of different atomic stacking sequences and periodicity along the *c* axis of these compounds.

To check the physical properties, we grew single crystals of MnBi_2Te_4 and MnBi_4Te_7 using a flux-assisted method, and found that it is difficult to synthesize these phases because they evolve only at a very narrow temperature range, similar to recent reports on the synthesis of single-crystalline MnBi_2Te_4 (18–21). The selected pieces of single crystals show shining surfaces and high quality, as indicated by the XRD patterns (Fig. 2). Compared to MnBi_2Te_4 , MnBi_4Te_7 has more complex diffraction peaks due to its more complex structure containing both QL and SL. The diffraction peak positions and intensities are in agreement with SAED results shown in Fig. 1, J and K. The fresh surfaces of the samples were checked by Auger electron spectroscopy and x-ray photoelectron spectroscopy under high vacuum (around 10^{-10} torr), and the results show that the samples are very clean and contain all the proposed elements, i.e., Mn, Bi, and Te (fig. S3). The content of Mn, which is the

magnetic center in MnBi_4Te_7 , is about half of the content in MnBi_2Te_4 (fig. S3D). This is consistent with the results that the former contains half QL and half SL, while the latter contains SL only.

Note that the preparation of $(\text{MnBi}_2\text{Te}_4)_m(\text{Bi}_2\text{Te}_3)_n$ with larger values of *m* (>2) and *n* (>1) would be rather challenging. The degree of difficulty for synthesis increases greatly from MnBi_2Te_4 to MnBi_4Te_7 and to $\text{MnBi}_6\text{Te}_{10}$, and we observed only a trace amount of $m = 3$, $n = 1$ phase in our solid-state reaction route for polycrystalline samples. For single-crystal growth, MnBi_2Te_4 evolves only at a narrow temperature interval (around 10°C from 590° to 600°C) (18–20), MnBi_4Te_7 evolves only within 2°C near 588°C , and the growth temperature for $\text{MnBi}_6\text{Te}_{10}$ is even narrower. Therefore, precise temperature controlling would be the most difficult point for growing the compounds with greater *m* and *n* values. Alternatively, on the basis of the present findings, deposition or transfer method might be feasible to prepare $(\text{MnBi}_2\text{Te}_4)_m(\text{Bi}_2\text{Te}_3)_n$ with any combination of *m* and *n*, although it is also challenging in skills.

The structural modifications are strongly indicative of modulations of the magnetic properties. We first measured the magnetization of polycrystalline MnBi_2Te_4 and a mixture of MnBi_4Te_7 and $\text{MnBi}_6\text{Te}_{10}$. The magnetization of MnBi_2Te_4 is consistent with a previous report (18), showing an AFM transition at $T_N = 25$ K and a spin-flop transition at 3.54 T (fig. S4, A and B). For the mixture of MnBi_4Te_7 and $\text{MnBi}_6\text{Te}_{10}$, magnetic susceptibility demonstrates an FM transition at $T_C = 12.1$ K for fields greater than 0.1 T (fig. S4, C to H).

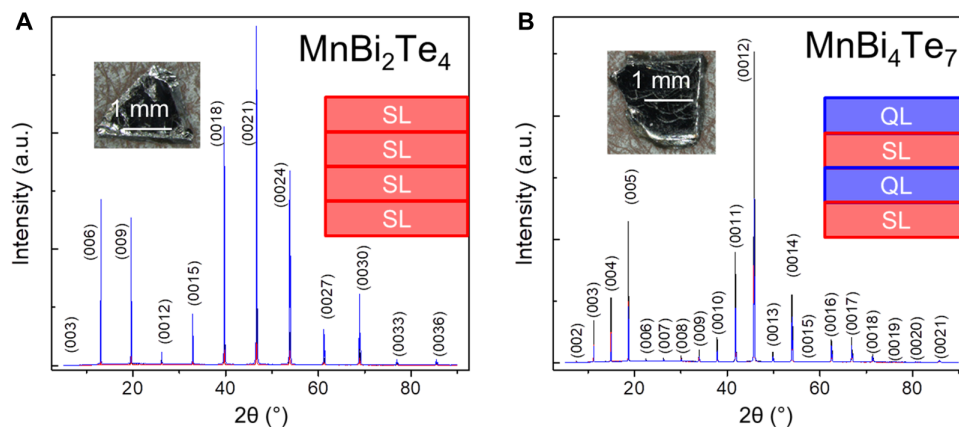


Fig. 2. XRD patterns of single crystals. (A) MnBi_2Te_4 . (B) MnBi_4Te_7 . The measurement was performed on single-crystalline pieces (shown in the insets) with only the a - b plane exposed to x-ray. The insets also show the structure models based on SL and QL van der Waals layers. a.u., arbitrary units.

However, for fields that are less than 0.1 T, there are two magnetic transitions: an AFM transition ($T_{N1} \cong 13$ K) attributed to MnBi_4Te_7 and a spin glass-like transition ($T_{N2} \cong 6.5$ K) probably attributed to $\text{MnBi}_6\text{Te}_{10}$ or amorphous phases (inhomogeneous QL and SL heterostructures). This field-dependent magnetization displays a saturation value at high fields and magnetic hysteresis at low fields below 5 K, indicating the arising of FM states.

To make the magnetic structures clear, we conducted magnetization measurements on single-crystalline MnBi_2Te_4 and MnBi_4Te_7 . The two compounds show remarkably different magnetic structures (Fig. 3). For MnBi_2Te_4 , the results are consistent with those for the polycrystalline sample, additionally demonstrating that the magnetization easy axis is along the c direction (10, 11, 19, 20). While the interlayer exchange coupling (IEC; which favors AFM states) of MnBi_2Te_4 is at an intermediate strength, the IEC of MnBi_4Te_7 becomes much weaker. For MnBi_4Te_7 , at a field of 1 T, the AFM transition disappears and an FM transition occurs at $T_C = 12.5$ K (Fig. 3D). The magnetization is saturated above 1 T for fields along either the c axis or the a - b plane (Fig. 3, E and F), indicating that the spin orientation can easily be realigned by an external field irrespective of the crystal orientation. However, similar to MnBi_2Te_4 , MnBi_4Te_7 also exhibits a magnetization easy axis along the c direction (fig. S5A).

Note that the AFM-IEC can still play an important role at small fields as shown in Fig. 3G and that an AFM transition takes place at $T_N = 12.7$ K. However, AFM-IEC seems not to be the only interaction that determines the magnetic order, because an obvious upturn was observed below T_N , especially for fields applied along the a - b plane. The first derivative of magnetic susceptibility over temperature also suggests that there might be another magnetic transition near 2 K (fig. S6, A to F). The field-dependent magnetization when a field is applied along the a - b plane shows a nonlinear curve below 5 K and a small hysteresis at 2 K (Fig. 3H), suggesting an additional magnetic interaction (AMI) that tends to cant the spins away from their out-of-plane direction and favors an FM state. When the field is applied along the z axis, we observed much higher hysteresis at 2 K with spin-flip transitions connecting FM phase at high fields and AFM phase at the critical field (H_c). The FM states can be maintained even at 0 T, indicating again the existence of AMI. However, the AMI decays rapidly with increasing thermal energy, and the magnetic hysteresis disappears above 5 K. Figure S6 provides a detailed analysis of the magnetic structure. We also observed the AFM transitions in MnBi_2Te_4 and MnBi_4Te_7

in their low-temperature heat capacities (figs. S5B and S7A). Note that because of the weak IEC, the magnetic properties of MnBi_4Te_7 can be modified by controlling the applied magnetic field (strength and direction). In addition, the IEC can be modified by controlling the spacers (QL), and it gradually decreases from MnBi_2Te_4 to MnBi_4Te_7 and to $\text{MnBi}_6\text{Te}_{10}$. In view of these features, we regard the magnetic properties of $(\text{MnBi}_2\text{Te}_4)_m(\text{Bi}_2\text{Te}_3)_n$ as “tunable.”

To gain insight into the electronic structure and topology of MnBi_4Te_7 , we carried out first-principles DFT calculations based on the hybrid functional (HSE06) method, which is used widely for the study of small bandgap materials. The obtained band structures, with and without spin-orbit coupling (SOC), of bulk MnBi_4Te_7 are shown in Fig. 4 (A and B, respectively). When SOC is turned off, Te-5 p states (valence bands) and Bi-6 p states (conduction bands) are separated by a direct gap of 633 meV at Γ point (Fig. 4A), consistent with their balanced charge states, $[\text{Bi}^{3+}]_2[\text{Te}^{2-}]_3$. However, this simple chemical picture breaks down when SOC is taken into account (Fig. 4B) with Te-5 p bands and Bi-6 p bands hybridizing near the Fermi level to cause band inversion (bandgap, 247 meV). This band inversion induced by strong SOC suggests that the material is topologically nontrivial (22). According to Mong *et al.* (23), AFM insulators breaking both time-reversal symmetry (Θ) and a primitive lattice translation symmetry ($T_{1/2}$) but preserving their combination $S = \Theta T_{1/2}$ (MnBi_4Te_7 is one such material) can be classified by \mathbb{Z}_2 topology. We carried out a Wilson loop calculation (24, 25) for MnBi_4Te_7 and confirmed that it is an AFM TI with $\mathbb{Z}_2 = 1$.

TIs are known to have SSs associated with their bulk topology (22). Figure 4 (C and D) shows the electronic structures of MnBi_4Te_7 slabs with two surface terminations, QL-terminated and SL-terminated, respectively. Distinct from the gapless SS in Bi_2Te_3 , the SSs of MnBi_4Te_7 are gapped with a gap of 11 meV (indirect) and 62 meV (direct) for the QL-terminated and SL-terminated surface, respectively. The non-vanishing gap is consistent with the broken time-reversal symmetry, presumably reflecting the interaction between the SSs and the FM layer near the surface, similar to the gapped SS of MnBi_2Te_4 (another AFM TI) (10, 19).

We measured the SS of MnBi_4Te_7 using ARPES at 20 and 300 K with an excitation photon energy of 48 eV (Fig. 5), which had been used for the experimental confirmation of the SS of Bi_2Te_3 , a prototypical three-dimensional TI (26). Closely resembling the SS of Bi_2Te_3 , while having a finite energy gap, the observed bands were confirmed to

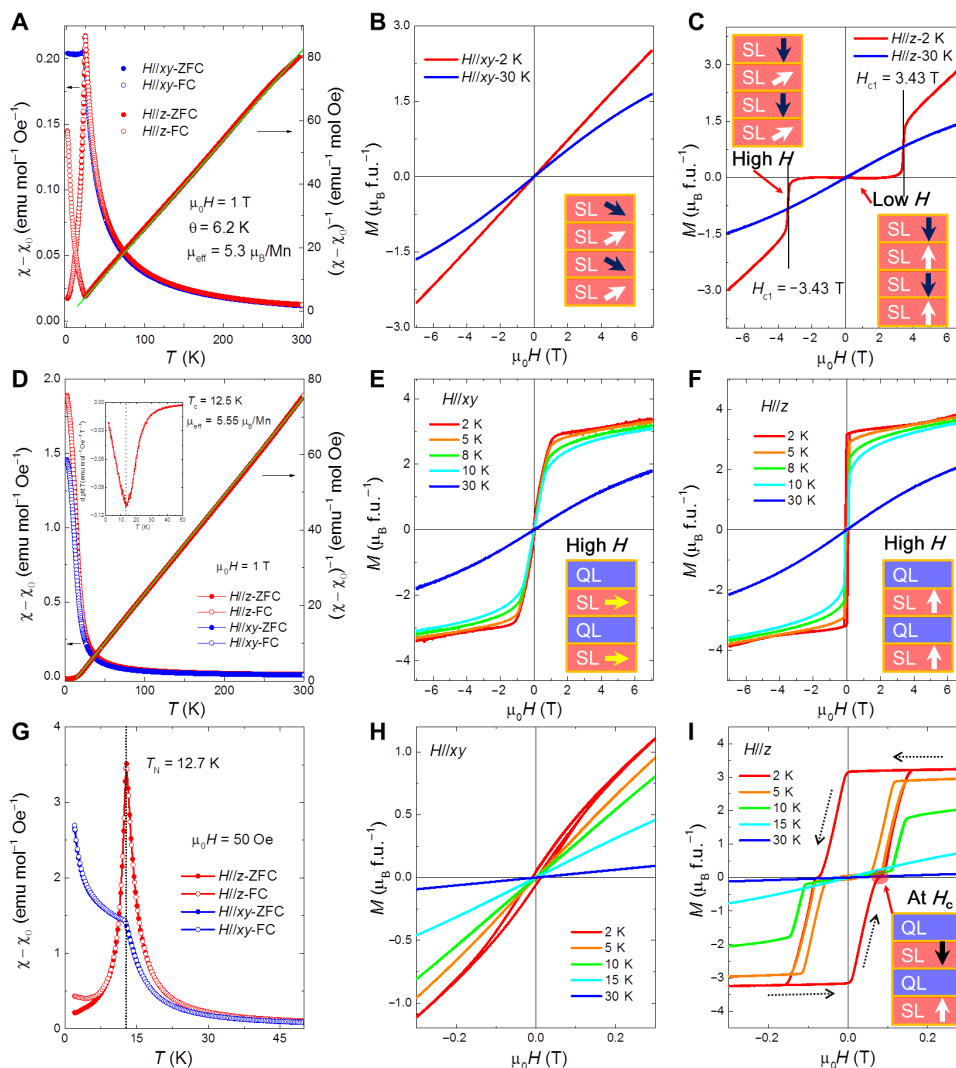


Fig. 3. Magnetic properties of MnBi₂Te₄ and MnBi₄Te₇ single crystals. (A to C) Magnetic susceptibility and magnetization of MnBi₂Te₄. The parameters θ and μ_{eff} are the Curie-Weiss temperature and effective moment, respectively. (D to F) Magnetic susceptibility and magnetization of MnBi₄Te₇ at high fields. (G to I) Magnetic susceptibility and magnetization of MnBi₄Te₇ at low fields. The black arrows with dotted lines in (I) show the sweep directions of the magnetic field. The heterostructures and spin structures are schematically shown as insets in (B), (C), (E), (F), and (I).

be SS, for which the $\bar{\Gamma}$ point was confirmed through measurements of the Fermi surface in the k_x - k_y plane (fig. S3, G and H). Compared with the calculation results (Fig. 4, C and D), the measured SSs (Fig. 5A) were found to come mainly from the SL-terminated surface as indicated by the bump (or cusp) at the valence band maximum. However, at the present stage, we cannot exclude the contributions from the QL-terminated surface, as it should be equally exposed on the mechanically cleaved surface (there are steps connecting QL and SL). Considering that the QL/SL surface domain size may be much smaller than the photon beam spot size in the present measurements, we speculate that both surfaces were measured. There are several possible reasons that the observed SSs look more like the contributions from SL, such as the self-protecting behavior of the topological states as proposed in a previous report (27) or a notably larger cross section of SL-SS than that of QL-SS. According to Fig. 4 (C and D), the contribution from the SL-terminated surface is much larger than that from the QL-terminated surface at the Γ point near the gap. This may be another reason that

we cannot resolve the two different types of surfaces, and the observed SS at the Γ point near the gap is mostly from SL. Given that the photon beam is only focused on QL, its SS would be largely enhanced and observable.

MnBi₄Te₇ exhibits surface bandgaps of 120 ± 10 and 90 ± 10 meV at 20 and 300 K, respectively (Fig. 5, B and D), similar to the reported data for MnBi₂Te₄ (10, 19). The opening of the surface bandgap above T_N (12.7 K) indicates that the time-reversal invariance is broken even in the paramagnetic (PM) phase for MnBi₄Te₇. Similar phenomena have been frequently observed in intrinsic magnetic TIs (10, 19) and magnetically doped TIs (28–31), but no consensus has been reached on the mechanism. Rader and co-workers (28) proposed that impurity-induced resonance states may destroy the Dirac point and explain the nonmagnetic gap, while this mechanism was excluded as the primary factor in MnBi₂Te₄ (a system similar to ours) (10). Mao and co-workers ascribed the PM gap to strong FM-type spin fluctuations (19). Actually, we have also observed FM spin fluctuations in

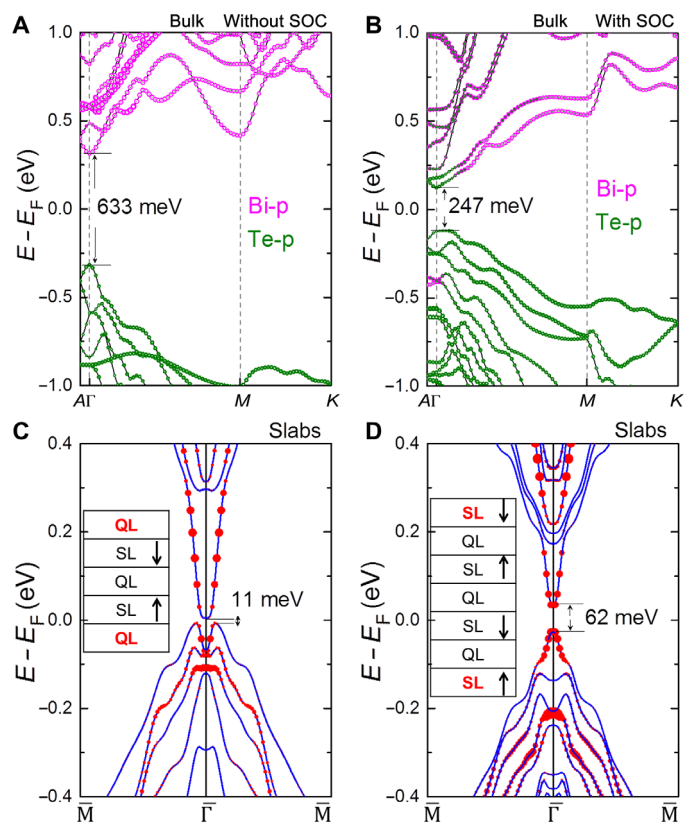


Fig. 4. DFT band structures of MnBi₄Te₇. (A) Bulk band structure without SOC. (B) Bulk band structure with SOC. (C) Band structure of a QL-terminated five-van der Waals layer slab. (D) Band structure of an SL-terminated seven-van der Waals layer slab. The calculations were performed assuming an AFM ground state. The thickness of the band is proportional to the contribution of the indicated atoms (A and B) or van der Waals layers [QL/SL in (C) and (D)].

MnBi₄Te₇ above T_N as indicated by the positive Curie-Weiss temperature (fig. S6, B and E); therefore, the present results may also suggest spin fluctuations as a possible reason for the SS gap. However, this is an open question requiring further investigations. A theory for the SS when the material is in the PM phase would be very helpful. Note that the SSs of MnBi₄Te₇ are more complex than those of MnBi₂Te₄, as indicated by a flattening of the conduction band and a cusp in the valence band near the $\bar{\Gamma}$ point (Fig. 5A), reminiscent of the more sophisticated SSs of PbBi₄Te₇ than that of PbBi₂Te₄ (27, 32). With gapped nontrivial SSs and tunable magnetic properties, magnetic heterostructures of $(\text{MnBi}_2\text{Te}_4)_m(\text{Bi}_2\text{Te}_3)_n$ will be an ideal platform for exploring tunable quantized magnetoelectric phenomena such as QAHE and axion insulator states.

The electrical transport properties of MnBi₄Te₇ single crystals are shown in Fig. 6, and they are notably different from those of MnBi₂Te₄ (fig. S7). The compound has a metallic conductivity (fig. S5C), and the Hall effect shows that the carrier is n-type with a carrier concentration (n) of $2.85 \times 10^{20} \text{ cm}^{-3}$ at 2 K (fig. S5D), consistent with the ARPES results that the Fermi level is not located in the SS Zeeman gap but in the conduction band (Fig. 5). The Hall resistivity has a linear field dependence at high fields (Fig. 6A), suggesting a single carrier in the present compound. The derived AH resistivity (Fig. 6A) is well coupled with the magnetization curves (Fig. 3I) and shows

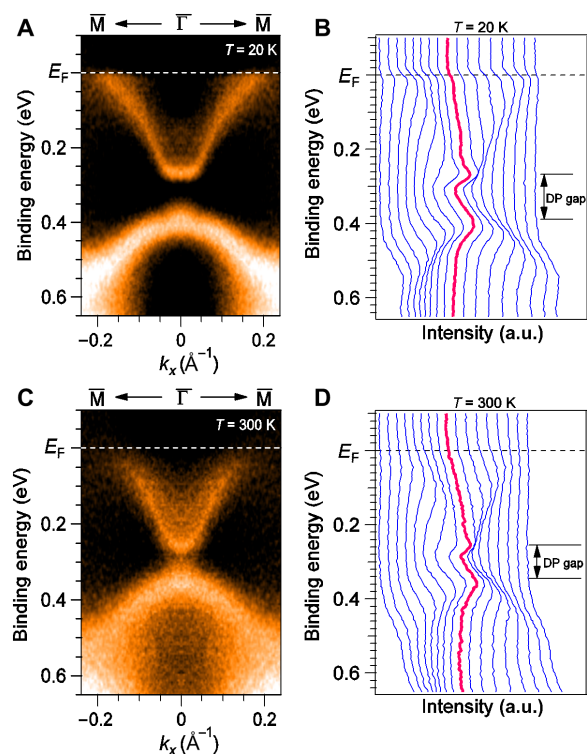


Fig. 5. Surface band structure of MnBi₄Te₇ at a photon energy of 48 eV. (A and C) Measured SS along the $\bar{\Gamma} - \bar{M}$ direction at 20 and 300 K, respectively. The intensity plots are symmetrized with respect to the center lines and averaged. (B and D) The energy distribution curves extracted from the intensity maps of (A) and (C), respectively, in the range of $-0.24 \text{ \AA}^{-1} < k_x < 0.24 \text{ \AA}^{-1}$. The intensity at the $\bar{\Gamma}$ point is shown in red. The DP in (B) and (D) is short for Dirac point.

hysteresis at low temperatures, which is strongly indicative of the possibility of observing QAHE if the Fermi level is tuned in the SS Zeeman gap (6, 7, 14). The AH conductivity, which can be expressed as $\sigma_{xy}^A = \rho_{yx}^A / \rho_{xx}^2$ (33), is shown to be virtually temperature independent below 2 K, while its temperature dependence above 2 K follows the same trend as magnetic susceptibility (Fig. 6, B and C). Here, ρ_{yx}^A and ρ_{xx} represent the AH resistivity and longitudinal resistivity, respectively. In general, there are three main mechanisms accounting for the AH effect, intrinsic Berry's phase curvature in the momentum space, side jump, and skew scattering (33). In the present study, the temperature-independent σ_{xy}^A and the scaling factor S_H ($\sigma_{xy}^A = S_H M$, M is the magnetization; Fig. 6C) and σ_{xx} -independent σ_{xy}^A (fig. S5F) exclude skew scattering as the primary reason and suggest that the intrinsic Berry's phase curvature is the major contribution to the AH effect (33–36). More studies are necessary for elucidation of the details. Note that a small nonlinear coupling of ρ_{yx}^A with M was observed below 5 K near the spin-flip transition (fig. S8) and the discrepancy ($\Delta\rho_H^A$) is n independent and probably due to the intrinsic contribution from the net Berry's curvature of a noncollinear spin texture (19, 37).

The spin-flip transitions can also be reflected in magnetoresistance (ρ_{xx}), as shown in Fig. 6 (D and E) and fig. S9. At higher temperatures (5 to 12 K), there are two peaks in ρ_{xx} at H_{c1} and H_{c2} , which are critical fields for spin-flip transitions with $H_{c2} = -H_{c1}$ (note that H_{c1} and H_{c2} are essentially the same and their signs only depend on the definition of the sign of the applied magnetic field). The sample is in AFM phase

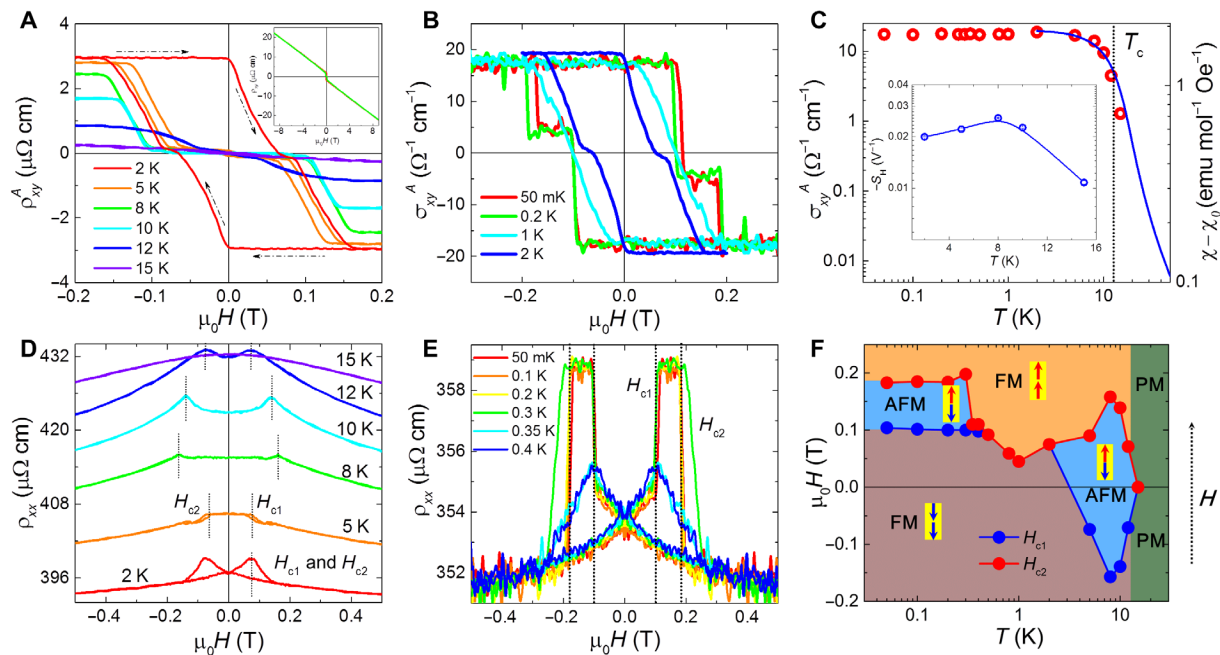


Fig. 6. Anomalous electrical transport properties and magnetic structures of MnBi_4Te_7 single crystals. (A) AH resistivity. The black arrows with dashed-dotted lines show the sweep directions of the magnetic field. The inset shows the total Hall resistivity at 2 K. (B) AH conductivity below 2 K. The central-symmetric data including background noise are due to the analysis method (see the Supplementary Materials). (C) Temperature dependence of AH conductivity and magnetic susceptibility measured at 1 T. The inset shows the temperature dependence of the scaling factor. (D) Field- and temperature-dependent magnetoresistance above 2 K. (E) Field- and temperature-dependent magnetoresistance below 1 K. (F) Temperature and field dependence of magnetic structures when the field is swept from a negative field to a positive field. Note that measurements above 2 K and below 1 K are on two pieces of samples. The magnetic field is applied along the c axis for all the transport properties measurements.

at a field between H_{c1} and H_{c2} and in FM phase at higher fields (Fig. 6F). At lower temperatures (50 mK to 2 K), H_{c1} and H_{c2} are on the same side (corresponding to the magnetic hysteresis of ρ_{yx}^A), either positive or negative, depending on the sweep direction of the field (Fig. 6F and fig. S5I), indicating that the sample turns into a spin valve-like state (1–3). H_{c1} and H_{c2} are nearly merged from 0.35 to 2 K (Fig. 6F), demonstrating that AFM states can survive only within a very narrow range of fields near the critical field. There are plateaus (high-resistance state) in ρ_{xx} between H_{c1} and H_{c2} at temperatures lower than 0.3 K (Fig. 6E), indicating that electrons suffer a higher scattering rate than they do at a lower or higher field. This implies that, different from the FM states at high fields (larger than H_{c2}), the material is now in an AFM state, similar to the phenomenon frequently observed for spin valves (1–3). However, the magnetoresistance plateaus cannot survive at higher temperatures (≥ 0.35 K), where thermal activation may destroy the AFM ordering quickly and the system enters an FM state. Although the FM state at a field between H_{c1} and H_{c2} should be more stable (in a lower energy level), it seems that the transition from AFM to FM cannot automatically happen (below 0.3 K) without sufficient thermal energy to overcome an energy barrier. This is supported by fig. S9E, where thermal activation for the transition from the high-resistance state (AFM) to the low-resistance state (FM) can be clearly observed (the resistance from 70 mK to 1 K at 0.15 T). Note that the plateaus are also shown in AH conductivity (Fig. 6B), resembling axion insulating states (8, 12, 14). Therefore, the present system is also a potential platform for creating axion insulators if the Fermi level is tuned into the SS Zeeman gap. In addition, when current flows across the magnetic and nonmagnetic layers, the

magnetoresistance effect seems much stronger (fig. S5H), similar to materials that show giant magnetoresistance (1, 4).

DISCUSSION

The field- and temperature-dependent magnetic structures of MnBi_4Te_7 are summarized in Fig. 6F and fig. S5I. The complex magnetic interactions indicate that MnBi_4Te_7 can be regarded as a magnetic order competing system. We can express the Hamiltonian regarding the spin structures in an applied magnetic field as $\mathcal{H} = \mathcal{H}_{\text{IEC}} + \mathcal{H}_{\text{AMI}} + \mathcal{H}_Z(B)$, where $\mathcal{H}_Z(B)$ is the Zeeman energy that depends on the field, B . As both \mathcal{H}_{IEC} and \mathcal{H}_{AMI} are small in the present system, only a small critical field is required to achieve a sufficient level of $\mathcal{H}_Z(B)$ to align the spins. The competition is mainly between \mathcal{H}_{IEC} terms that favor the AFM states and \mathcal{H}_{AMI} terms that favor the FM states, and the AFM states are found to be metastable (fig. S9E). Both \mathcal{H}_{IEC} and \mathcal{H}_{AMI} are weakened with increasing temperature; however, \mathcal{H}_{AMI} decays much faster than \mathcal{H}_{IEC} . The energy difference obtained by DFT calculations between the FM and AFM states is only $\epsilon(\text{FM}) - \epsilon(\text{AFM}) = 0.44$ meV per Mn ion, comparable to a thermal energy of 5 K (see the Supplementary Materials). This small energy difference strongly indicates the possibility of competing FM and AFM states in the present material. There are several candidates for AMI: Ruderman-Kittel-Kasuya-Yosida interaction mediated by conduction carriers (38), Dzyaloshinskii-Moriya interaction due to the breakdown of inversion symmetry (39), and van Vleck mechanism-mediated FM interaction, as reported in diluted magnetic doped TI (40). However, further investigation is needed to determine the

exact mechanism. Note that this competing situation is not found in MnBi_2Te_4 (fig. S7E), in which the AFM-IMC is much stronger and may exceed the AMI. Therefore, the competing magnetic order in MnBi_4Te_7 may induce unexplored topological states.

In summary, the exotic magnetic structures of the present materials will not only lead to fundamental interests in magnetism but also provide a new platform (by combining the non-trivial SSs) for topotronics toward quantized magnetoelectric phenomena. In addition, successful isolation of the van der Waals materials will provide brand new opportunities to study the interplay between magnetism and topology down to two-dimensional limits (41).

MATERIALS AND METHODS

Crystal growth

Polycrystalline samples of MnBi_2Te_4 and a mixture of MnBi_4Te_7 and $\text{MnBi}_6\text{Te}_{10}$ were synthesized using a solid-state reaction route. Stoichiometric amounts of the elements (Mn:Bi:Te, 1:4:7 for the mixture) were loaded inside a carbon-coated silica tube and sealed under vacuum and then pretreated using a hydrogen flame. The fused ingot was crushed, ground into a powder, and pelleted inside an Ar-filled glove box. Then, the pellet was sealed in vacuum inside a carbon-coated silica tube and annealed at 550°C for 5 days and lastly water-quenched. For the growth of MnBi_2Te_4 and MnBi_4Te_7 single crystals, a similar procedure was performed before heating in a furnace. The starting element composition ratio was Mn:Bi:Te = 1:6:10 in both cases. Further reduction of Mn content also worked well. The key point for the synthesis is controlling the growth temperature, which was reported to be as narrow as 10°C (17–20). The present synthesis was conducted by heating it up to 1000°C and maintaining it for 3 hours, cooling it down to 600°C for 10 hours, then cooling it to T_{end} over 1 week, and lastly quenching it using ice-cold water. T_{end} should be above the melting point of Bi_2Te_3 . It was set to 590°C for the growth of MnBi_2Te_4 and 588°C for MnBi_4Te_7 . The growth method can be regarded as a flux (Bi_2Te_3) method (20). Single crystals with laminated structures were peeled and cleaved from the grown bulks. As the quenching temperature was higher than the melting point of Bi_2Te_3 , no Bi_2Te_3 single-crystal pieces could be found. The Bi_2Te_3 obtained after quenching showed bad crystallinity, as indicated by broad and asymmetric XRD peaks.

Sample characterization

Powder XRD measurements were performed using an x-ray powder diffractometer with Cu $K\alpha$ radiation (Bruker D8 ADVANCE), and the results were refined using the GSAS package (42). Auger electron spectra were obtained with 10-keV primary electrons using a Scanning Auger Nanoprobe System (PHI 710, ULVAC-PHI). HAADF-STEM images were obtained using a JEOL JEM-ARM200F atomic resolution analytical electron microscope operated at an accelerating voltage of 200 kV. To observe the lattice periodicity along the c direction, TEM specimens were prepared using the ion milling technique. First, the powder was mixed with epoxy resin and loaded into a stainless pipe with a diameter of 3 mm. Then, the pipe was thinned by mechanical polishing and dimpling until the central part reached a thickness of 40 μm . Last, it was further thinned by ion milling using 4-keV Ar ions.

Physical properties measurements

Magnetization was measured using a Magnetic Property Measurement System (MPMS SQUID VSM Quantum Design). Electrical transport

properties (resistance, magnetoresistance, and Hall resistance) and heat capacity measurements above 2 K were performed using a Physical Properties Measurement System (Quantum Design). The electrical transport properties below 1 K were measured using a ^3He - ^4He dilution refrigerator. For the measurements of the electrical transport properties, the magnetic field was applied along the c axis of the van der Waals crystals.

Surface band structure characterization

ARPES measurements were carried out using horizontally polarized synchrotron radiation light at the BL-2A MUSASHI beam line of the Photon Factory, KEK. Samples were cleaved in situ under an ultra-high vacuum of 1×10^{-10} torr, and the experimental data were collected using a Scienta SES-2002 electron energy analyzer. The sample temperature during the ARPES measurements was set to 20 and 300 K, with a total energy resolution of 30 meV at a photon energy ($h\nu$) of 48 eV. The size of the photon beam was around 300 μm in diameter.

Theoretical calculations

Ab initio electronic structure calculations were carried out using the projector augmented wave method with a plane wave basis, as implemented in the Vienna ab initio simulation package (43, 44). The exchange-correlation potential was treated in the screened Heyd-Scuseria-Ernzerhof hybrid functional scheme in the HSE06 parameterization (45, 46). The plane waves were cut off at 350 eV, while the k -sampling mesh was chosen to be $6 \times 6 \times 2$ and $5 \times 5 \times 1$ for bulk and slabs, respectively. The Wilson loop calculation to determine the topological index was carried out using a tight-binding Hamiltonian in the Wannier function basis derived from the ab initio calculation (24, 25). The ground state of the system was assumed to be AFM.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/5/11/eaax9989/DC1>

Section S1. Data analysis methods for electrical transport measurements

Fig. S1. Crystal structures and XRD patterns.

Fig. S2. Additional STEM data.

Fig. S3. Additional surface characterization.

Fig. S4. Magnetization of polycrystalline samples.

Fig. S5. Additional physical properties of MnBi_4Te_7 single crystals.

Fig. S6. Additional information for the magnetization of MnBi_4Te_7 single crystals.

Fig. S7. Additional physical properties of MnBi_2Te_4 single crystals.

Fig. S8. Magnetization dependence of ρ_{xx}^A for MnBi_4Te_7 single crystals.

Fig. S9. Additional electrical transport properties below 1 K for MnBi_4Te_7 single crystals.

Table S1. Crystal structure parameters of Mn-Bi-Te compounds.

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Natural van der Waals heterostructural single crystals with both magnetic and topological properties

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