A-type Antiferromagnetic order in MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$ single crystals

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MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$ are two members with n=2 and 3 in the family of MnBi$_{2n}$Te$_{3n+1}$ where the n=1 member, MnBi$_2$Te$_4$, has been intensively investigated as the first intrinsic antiferromagnetic topological insulator. Here we report the A-type antiferromagnetic order in these two compounds by measuring magnetic properties, electrical and thermal transport, specific heat, and neutron single crystal diffraction. Both compounds order into an A-type antiferromagnetic structure as does MnBi$_2$Te$_4$ with ferromagnetic planes coupled antiferromagnetically along the crystallographic c axis. The ordering temperature, $T_N$, is 13 K for MnBi$_4$Te$_7$ and 11 K for MnBi$_6$Te$_{10}$, respectively. The magnetic order is also manifested in the anisotropic magnetic properties. For both compounds, the interlayer coupling is weak and a spin flip transition occurs when a magnetic field of around 1.6 kOe is applied along the c-axis at 2 K. At 2 K and in a magnetic field of 70 kOe, the saturation moment is 3.16$\mu_B$/Mn for MnBi$_4$Te$_7$ and 3.62$\mu_B$/Mn for MnBi$_6$Te$_{10}$. As observed in MnBi$_2$Te$_4$, when cooling across $T_N$, no anomaly was observed in the temperature dependence of thermopower, however, a critical scattering effect is observed in thermal conductivity although the effect is less pronounced than that in MnBi$_2$Te$_4$.

INTRODUCTION

The antiferromagnetic topological insulators$^1$ can be an ideal materials playground for the study of various topological quantum phenomena, including the quantum anomalous Hall effect and quantum axion electrodynamics. Recently, a layered cleavable transition metal chalcogenide, MnBi$_2$Te$_4$, was proposed$^2$, $^3$ to be the first intrinsic antiferromagnetic topological insulator. As shown in Figure 1, the rhombohedral crystal structure of MnBi$_2$Te$_4$ has an A-B-C stacking along the crystallographic c-axis of the septuple layers which can be viewed as inserting one Mn-Te layer into a quintuple layer (see Figure 1(b)). MnBi$_2$Te$_4$ is one member of a family compound with the chemical formula MnBi$_{2n}$Te$_{3n+1}$ and has n=1. Further spacing the magnetic septuple layers by the nonmagnetic quintuple layers along the c-axis can lead to other MnBi$_{2n}$Te$_{3n+1}$ members with n≥2. Previous experimental studies suggest the presence of compounds with n up to 5$^4$, $^6$. Figures 1 (d,e) show the stacking of the septuple and quintuple layers along the c-axis for MnBi$_4$Te$_7$ (n=2) and MnBi$_6$Te$_{10}$ (n=3).

Compared to MnBi$_2$Te$_4$, n=2 members have two unique features: (1) the magnetic septuple layers are further separated, which reduces the interlayer coupling, $J_c$. If the single ion anisotropy, D, is less affected, the reduced $J_c$ would significantly modify the magnetic response to the external field as observed in MnBi$_{2−}$_Sb$_2$Te$_6$,$^7$; (2) The termination layer can be the magnetic septuple layers or the nonmagnetic quintuple layer. Thus quite different surface states can be expected. In addition, the termination quintuple layer might behave as a natural capping layer and affect the magnetic and electronic properties of the septuple layer right beneath it. Different stacking of the septuple and quintuple layers enriches the topological phenomena expected in MnBi$_{2n}$Te$_{3n+1}$ compounds.$^8$

MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$ have been theoretically proposed to be a possible materials platform for the chiral Majorana fermion.$^9$ The magnetic and transport properties, and the electronic structure of MnBi$_4$Te$_7$ have been experimentally investigated on single crystals by three different groups$^{10}$-$^{12}$. While all report an antiferromagnetic order below $T_N$=13 K, Mn deficiency seems to introduce one extra magnetic order around 5 K which further enriches the topological phase diagram$^{12}$. The anisotropic magnetic properties suggest the ordered moment is along the crystallographic c-axis. An A-type antiferromagnetic structure is likely while a neutron diffraction confirmation is still absent. The magnetic measurements on a polycrystalline MnBi$_6$Te$_{10}$ suggests a ferromagnetic order with $T_c$=12 K.$^5$. An investigation of the intrinsic and anisotropic properties using single crystal samples is still needed.

In this work, we report the magnetic, transport, and thermodynamic properties of MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$ single crystals. We also report the magnetic structure determined by neutron single crystal diffraction. Magnetic order above 10 K persists even though the c-axis distance between interlayers of Mn approaches dozens of Angstroms. Both compounds order into an A-type antiferromagnetic structure as does MnBi$_2$Te$_4$. The magnetic ordering temperature of 13 K for MnBi$_4$Te$_7$ is slightly higher than 11 K for MnBi$_6$Te$_{10}$. In both compounds, the interlayer coupling $J_c$ is significantly reduced by the increased spacing in between the magnetic septuple layers and is much weaker than the single ion anisotropy. Therefore, as in MnSb$_2$Te$_4$, a small magnetic field of 1.6 kOe along the c-axis is enough to flip the moments at 2 K.
EXPERIMENTAL DETAILS

MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$ single crystals were grown out of a Bi-Te flux using the same starting materials and cooling process as for the growth of MnBi$_2$Te$_4$\cite{12}. According to the phase diagram developed by Aliev et al.\cite{6}, MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$ should crystallize at a lower temperature than that for MnBi$_2$Te$_4$. The crystallization of MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$ using the same growth procedure for MnBi$_2$Te$_4$ might result from a natural temperature gradient of the box furnace. However, the flux can be well separated from crystals by decanting in a centrifuge at a set up temperature of 585°C. While further study is needed to reveal the growth mechanism, we noticed that an overnight dwelling at 595°C seems to favor the crystallization of MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$ and the growth is even reproducible.

Figures 2 (a) and (b) show the pictures of the plate-like crystals. It is interesting to note that MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$ crystals grown in this manner tend to be rather thick (typically over 1 mm). Elemental analysis on cleaved surfaces was performed to determine the elemental ratio using a Hitachi TM-3000 tabletop electron microscope equipped with a Bruker Quantax 70 energy dispersive x-ray system. Some small crystals were ground together with fine power of silicon\cite{7,14} for x-ray powder diffraction measurements, which were performed at room temperature using a PANalytical X’Pert Pro diffractometer with Cu-K$_\alpha1$ radiation.

Magnetic properties in fields up to 70 kOe were measured with a Quantum Design (QD) Magnetic Property Measurement System (MPMS). Magnetization data in fields up to 120 kOe were collected using the ac option of a 14 Tesla QD Physical Property Measurement System (PPMS). The temperature and field dependent electrical resistivity data were collected using a 9 Tesla QD Physical Property Measurement System (PPMS). The temperature dependence of thermal conductivity and thermopower data were collected using the TTO option of 9 Tesla PPMS on rectangular bars with the dimensions of 1.2 mm $\times$ 0.75 mm $\times$ 7 mm cut from a large plate-like crystals. Silver epoxy (H20E Epo-Tek) was utilized to provide mechanical and thermal contacts during the thermal transport measurements. The thermal conductivity measurement was performed with the heat flow in the ab-plane.

Single crystal neutron diffraction experiments at temperatures down to 6.5 K were carried out at the CORELLI spectrometer\cite{15} at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory. CORELLI is a quasi-Laue time-of-flight instrument equipped with a large 2D detector, with a $-20^\circ$ to $+150^\circ$ in-plane coverage and $\pm 28^\circ$ out-of-plane coverage. The incident neutron wavelength is between 0.65 Å and 2.9 Å. The sizes of the two plate-like crystals used in the experiment are about $4 \times 5 \times 1$ mm$^3$ for MnBi$_4$Te$_7$ and $3 \times 4 \times 0.6$ mm$^3$ for MnBi$_6$Te$_{10}$, respectively. Both samples were mounted with the c-axis in the horizontal plane. Neutron-absorbing Cd was used to shield the sample holder to reduce the background scattering. Experiments were conducted by rotating the sample through a 180° range with a 2° step at both below and above the magnetic transition temperatures to better isolate the magnetic Bragg scattering contributions. Order-parameter type data were collected as a function of temperature at a few fixed angles optimized for signals from particular magnetic peaks of interest. The Mantid package was used for data reduction including Lorentz and spectrum corrections\cite{16}. The integrated Bragg intensities were obtained from integration in the 3D reciprocal space and were corrected for background. Possible magnetic structures were investigated by representation analysis using the SARAh program\cite{17} and by the magnetic symmetry approach using the MAXMAG program available at the Bilbao Crystallographic Server\cite{18}. The magnetic structural refinements were carried out with the FullProf Suite program\cite{19}.

RESULTS

Elemental analysis and X-ray

The elemental analysis was performed on flat surfaces cleaved in air. Multiple pieces from each batch were checked and no composition variation was observed. The measurements give a composition of Mn$_{6.8}$Bi$_{34.5}$Te$_{58.7}$ for the nominal MnBi$_4$Te$_7$. This suggests the MnBi$_4$Te$_7$ crystals are Bi rich and can also have Mn vacancy. With the assumption that extra Bi occupy the Mn site, the chemical formula can be written as (Mn$_{0.81}$Bi$_{0.12}$)$\square$Bi$_{0.78}$Te$_7$. This composition is similar to that reported by Vidal et al.\cite{12}. As presented later, our MnBi$_4$Te$_7$ crystals also order antiferromagnetically at $T_N$=13 K, the same as previous reports\cite{10}.

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Figure 1. (color online) The structure units: (a) The quintuple layer, (b) the septuple layer. The crystal structure of (c) MnBi$_2$Te$_4$, (d) MnBi$_4$Te$_7$, and (e) MnBi$_6$Te$_{10}$.
FIG. 2. (color online) The pictures of single crystals of (a) MnBi$_4$Te$_7$ and (b) MnBi$_6$Te$_{10}$. (c) (00$l$) reflections of MnBi$_4$Te$_7$ suggesting the c-axis is perpendicular to the plane of the plate. (d) (00$l$) reflections of MnBi$_6$Te$_{10}$. The reflections are indexed with the structure proposed in Ref[6]. Weak reflections from Bi$_2$Te$_3$ in (c,d) and MnBi$_4$Te$_7$ in (d) are also indexed.

The elemental analysis for the nominal MnBi$_6$Te$_{10}$ crystals gives a composition of Mn$_{4.4}$Bi$_{36.6}$Te$_{75.0}$, corresponding to (Mn$_{0.75}$Bi$_{0.25}$)$_{0.05}$Bi$_6$Te$_{10}$. For simplicity, we still label the crystals as MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$ in the following text. The elemental analyses suggest significant amount of Bi at Mn site. With the above nonstoichiometry and occupancy, both compounds are expected to be n-type, which is confirmed by the Hall measurements presented later. It should be noted that MnBi$_2$Te$_4$ crystals grown using the same procedure tend to be stoichiometric[12]. Considering the growths of all three compounds start with the same starting materials, the Mn deficiency observed in MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$ crystals indicates that a small percentage of Mn in Bi$_2$Te$_3$ flux can lower the melting temperature of the flux or the diffusivity of Mn in the melt is rather sensitive to temperature and plays an important role in selecting the precipitation.

Figures 2(c) and (d) present the XRD patterns of the plate-like single crystals along the c-axis of MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$. The (00$l$) reflections can be indexed with the structure proposed in Ref[6]. It is interesting to note that a few weak reflections from Bi$_2$Te$_3$ are observed for both compounds. Also observed in Figure 2(d) is the (104) reflection from MnBi$_4$Te$_7$. This suggests possible intergrowth of MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$ in the crystal. The rather weak reflections from Bi$_2$Te$_3$ and MnBi$_4$Te$_7$ are also observed in the powder diffraction pattern (not shown) taken on pulverized MnBi$_6$Te$_{10}$ crystals. Considering the complex stacking along the c-axis in MnBi$_6$Te$_{10}$, the intergrowth is not a surprise, and it is expected that the amount of stacking disorder might increase with increasing n in the MnBi$_2n$Te$_{3n+1}$ series. While a small fraction of stacking disorder may not significantly alter the bulk properties, it may affect the results in surface sensitive measurements such as angle resolved photoemission spectroscopy or scanning tunneling microscopy, and may dominate the

FIG. 3. (color online) Temperature dependence of magnetic susceptibility in an applied magnetic field of 250 Oe perpendicular (H//ab) and parallel (H//c) to the crystallographic c axis for (a) MnBi$_4$Te$_7$ and (b) MnBi$_6$Te$_{10}$.
transport properties of thin flakes which happen to have stacking defects.

Since a decent refinement of the powder diffraction pattern cannot be obtained, we estimated the volume fraction of MnBi$_4$Te$_7$ in the the MnBi$_6$Te$_{10}$ crystals to be around 3% by simply comparing the intensity of the strongest peak of each phase. Using the structure model reported previously[5, 6], the lattice parameters at room temperature are a=4.3658 Å, c=23.80 Å for MnBi$_4$Te$_7$, and a=4.374 Å, c=101.93 Å for MnBi$_6$Te$_{10}$, which are in good agreement with previous reports[5, 6].

Magnetic properties

Figure 3 shows the temperature dependence of the magnetic susceptibility measured in an applied magnetic field of 250 Oe applied perpendicular (labelled as H//ab) and parallel (H//c) to the crystallographic c-axis. MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$ show similar anisotropic temperature dependent magnetic susceptibility. The anisotropic temperature dependence suggests an antiferromagnetic order and the ordering temperature is $T_N=13$ K for MnBi$_4$Te$_7$ and $T_N=11$ K for MnBi$_6$Te$_{10}$. $T_N=13$ K for MnBi$_4$Te$_7$ agrees with previous reports[10–12]. For both compounds, the magnetic susceptibility curves measured with H//ab and H//c in the temperature range 50≤T≤300 K can be described by the Curie-Weiss law, $\chi = C/(T - \theta)$, where C is the Curie constant and $\theta$ is the Weiss temperature. The Curie-Weiss fitting of the high temperature susceptibility data of MnBi$_6$Te$_{10}$ obtains a Weiss temperature of 12 K and an effective moment of 5.0(1)$\mu_B$/Mn. A similar fitting for MnBi$_4$Te$_7$ obtains a Weiss temperature of 11 K and an effective moment of 5.2(1)$\mu_B$/Mn. The positive Weiss temperature suggests ferromagnetic correlations in the paramagnetic state despite the low temperature antiferromagnetic order. It is worth mentioning that all n=1,2, and 3 members have a positive Weiss temperature even though they all order antiferromagnetically at low temperatures. The Curie-Weiss-like tail below $\approx$8 K in the temperature dependence of magnetic susceptibility of MnBi$_4$Te$_7$ is different from a nearly temperature independent susceptibility for MnBi$_4$Te$_7$. We carefully cleaned the crystal surface and edges to reduce the possible contribution from magnetic impurities[13]. However, the Curie-Weiss-like tail is always observed. This Curie-Weiss-like tail is also observed in two previous reports[10, 11]. Whether the low-temperature Curie-Weiss-like feature is an intrinsic property of MnBi$_4$Te$_7$ deserves further study. We noticed that the composition of our MnBi$_4$Te$_7$ single crystals is similar to that reported by Vidal et al[12]. However, the magnetic properties are different especially below 5 K. The difference might result from the concentration and/or distribution of Mn/Bi antisite defects.

Figure 4 shows the magnetization, M(H), curves at 2 K in fields up to 70 kOe applied both along and perpendicular to the crystallographic c axis. For both compounds, a spin flip transition occurs around a field of 1.6 kOe when the field is parallel to the c axis (H//c). Once the field is applied perpendicular to the c axis (H//ab), the magnetization increases with field and then tends to saturate above 10 kOe. The field dependence of magnetization resembles that of MnSb$_2$Te$_4$[7]. As discussed later, this is because the interlayer coupling is significantly reduced by the increased spacing between the magnetic layers while the single ion anisotropy remains more or less unchanged compared to that in MnBi$_2$Te$_4$. We would also point out that two extra weak features are observed in the magnetization curves shown in Fig. 4. (1) In between 40-50 kOe, the magnetization shows an about 10% increase and no hysteresis was observed in this field range. It is interesting to note that this 10% enhancement occurs in both compounds and for both H//c and H//ab.
it originates from an impurity phase, the isotropic behavior might signal a polycrystalline impurity or a soft magnetic impurity. (2) The other feature that should be noted is the steps in M(H) curves around zero magnetization which are highlighted in insets of Fig. 4. The origin of this anomaly is unknown and it might be correlated with the 10% enhancement at high fields. The origin of both features deserves further study.

At 70 kOe and 2 K, the saturation moment is $3.16 \mu_B/Mn$ for MnBi$_4$Te$_7$ and $3.62 \mu_B/Mn$ for MnBi$_6$Te$_{10}$. No other field induced transitions are observed up to 120 kOe (data not shown).

**Transport properties**

Figure 5 shows the temperature and field dependence of the in-plane electrical resistivity measured in the temperature range 2 K $\leq$ T $\leq$ 300 K. Both compounds show a metallic conducting behavior and a cusp around $T_N$. Compared to MnBi$_2$Te$_4$, both compounds are more conductive. Inset of Fig. 5 highlights the details around $T_N$ and also the effect of a magnetic field of 80 kOe applied along the crystallographic c-axis. Both the temperature and field dependence of both compounds resembles that of MnBi$_2$Te$_4$.

Figure 6(a) shows the Hall resistivity at selected temperatures. A linear field dependence is observed at all temperatures for both compounds. The Hall coefficient shows little temperature dependence below room temperature. With the assumption that a single band dominates the Hall signal, the room temperature coefficient gives an electron density of $6.0 \times 10^{20} \text{cm}^{-3}$ and $3.5 \times 10^{20} \text{cm}^{-3}$ for MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$, respectively. Figure 6(b) shows the field dependence of in-plane $\rho_{xx}$ and $\rho_{xy}$ at 2 K in magnetic fields up to 80 kOe applied along the c-axis. While a linear field dependence of $\rho_{xy}$ is observed for both compounds, $\rho_{xx}$ decreases with increasing field reaching a minimum around 20 kOe and 10 kOe for MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$, respectively, then increases slightly with increasing field. The slight increase of $\rho_{xx}$ at high fields is similar to that of MnSb$_2$Te$_4$ and is typical for a metal.

Figure 7(a) shows the temperature dependence of the in-plane thermal conductivity, $\kappa(T)$, in the temperature range 2 K $\leq$ T $\leq$ 250 K. $\kappa(T)$ curves for both compounds show a maximum around 30 K and little temperature dependence above 50 K, similar to that of MnBi$_2$Te$_4$. Around 250 K, MnBi$_4$Te$_7$ has an in-plane thermal conductivity of $\approx 4.8 \text{W/K m}$, which is about 50% larger than
FIG. 7. (color online) (a) Temperature dependence of in-plane thermal conductivity in the temperature range 2 K ≤ T ≤ 250 K. The electronic thermal conductivity, \( \kappa_e \), was estimated from the electrical resistivity data using the Wiedemann-Franz law. The lattice thermal conductivity, \( \kappa_{ph} \), was obtained by subtracting \( \kappa_e \) from the total thermal conductivity. (b) Details of the in-plane thermal conductivity around \( T_N \). \( \kappa_4 \) is the thermal conductivity for MnBi\(_4\)Te\(_7\). \( \kappa_6 \) is the thermal conductivity for MnBi\(_6\)Te\(_{10}\).

FIG. 8. (color online) Temperature dependence of thermopower.

Figure 8 shows the temperature dependence of thermopower, \( \alpha(T) \), below room temperature. At room temperature, \( \alpha(T) \) has a value of -38 \( \mu \)V/K and -26 \( \mu \)V/K for MnBi\(_4\)Te\(_7\) and MnBi\(_6\)Te\(_{10}\), respectively. The negative sign of \( \alpha(T) \) signals electrons dominated charge transport, consistent with the Hall data. The absolute value of \( \alpha(T) \) decreases upon cooling from room temperature to 2 K. The nearly linear temperature dependence above 50 K corresponds to the characteristic diffusion thermopower of a metal. Similar to that in MnBi\(_2\)Te\(_4\), no response of \( \alpha(T) \) to the magnetic order was observed around \( T_N \).

Specific heat

Figure 9 shows the temperature dependence of specific heat below 200 K for MnBi\(_4\)Te\(_7\) and MnBi\(_6\)Te\(_{10}\). The data for MnBi\(_2\)Te\(_4\) is also plotted for comparison. The specific heat data approach the Dulong-Petit limit at high temperatures. As highlighted in the insets of the figure, there is a weak lambda-type anomaly around \( T_N \) for each composition and the magnitude of the anomaly becomes smaller with increasing \( n \). The weak anomaly around \( T_N \) might result from the entropy release by the two dimensional (2D) magnetic correlations existing at higher temperatures as reported in other 2D cleavable magnets\(^{20, 21}\). The low temperature specific heat data in the range 10 ≤ \( T^2 \) ≤ 60 K\(^2\) can be follow the standard power law, \( C_P = \gamma T + \beta T^3 \), where \( \gamma \) is the Sommerfeld electronic specific heat coefficient and \( \beta \) is the coefficient of the Debye \( T^3 \) lattice heat capacity at low temperatures. The fitting of the low temperature specific heat data gives the \( \gamma \) value of 0.18, 0.34, and 0.67 J/mol K\(^2\) for MnBi\(_2\)Te\(_4\), MnBi\(_4\)Te\(_7\), and
MnBi$_6$Te$_{10}$, respectively. Debye temperature, $\theta_D$, can be estimated from the $\beta$ coefficient using the following equation 

$$\theta_D = (12\pi^4 N_A k_B n / 5\beta)^{1/3},$$

where $n$ is the number of atoms per formula unit, $N_A$ is Avogadro’s constant and $k_B$ is Boltzmann’s constant. All three compounds have a similar $\theta_D$, which is 110, 120, and 120 K for MnBi$_2$Te$_4$, MnBi$_4$Te$_7$, and MnBi$_6$Te$_{10}$, respectively.

Neutron single crystal diffraction

Magnetic Order and Critical Behavior

Figure 10 shows the slice cuts in the H0L plane of the single-crystal neutron diffraction data from MnBi$_4$Te$_7$, collected at 6 K and 20 K, respectively. Comparing to the 20 K data, there are additional Bragg peaks at half-integer-L positions in the low Q regions at 6 K. These half-integer-L Bragg peaks become less visible as $L$ increases, indicating that they are originated from scattering of the ordered magnetic moments. The locations of these peaks agree with a magnetic wavevector of (0 0 0.5), suggesting that the magnetic unit cell is twice as large as the chemical unit cell along the $c$-axis. Note that these half-integer-L Bragg peaks are absent along the [0 0 L] direction. Due to the vectorial nature of the neutron-magnetic moment interaction [22], the absence suggests that the ordered magnetic moment is along the $c$-axis, consistent with the anisotropic magnetic properties.

Figures 11(a) and 11(b) show the similar slice cuts from the MnBi$_6$Te$_{10}$ datasets collected at 6 K and 18 K, respectively. New features along L in the [1 0 L] direction show up at 6 K when cooling down from 18 K. However, as seen from the 18 K dataset, the nuclear Bragg peaks have very long tails in the L direction. To better isolate the new scattering features, the difference between the two datasets are shown in Fig. 11(c). It becomes clear that the new features are Bragg-peak-like and located at positions of (1 0 3N-0.5), where N is an integer. The locations of these new peaks agree with a magnetic wavevector of (0 0 1.5). Similar to MnBi$_4$Te$_7$, these are no detectable half-integer-L Bragg peaks along the [0 0 L] direction, therefore the ordered magnetic moment is along the $c$-axis for MnBi$_6$Te$_{10}$ too.

Figure 12 shows the temperature dependence of the selected low Q magnetic Bragg peaks. The 2D plots show that the high temperature background is very clean for MnBi$_4$Te$_7$, but high for MnBi$_6$Te$_{10}$. As discussed above, the high background for MnBi$_6$Te$_{10}$ is from the tails of the adjacent nuclear Bragg Peaks. This has some effects on the peak intensity integration for the magnetic structure determination, which will be discussed later. Here we assume that the high temperature background is temperature independent and fit the temperature dependence of the integrated magnetic peak intensities below $T_N$ using the scaling equation of state, 

$$I(T) = I_0 \times (1 - T/T_N)^{2\beta} + I_{bac},$$

where $\beta$ is the critical exponents, $T_N$ is the magnetic ordering temperature, and $I_{bac}$ is a constant background. The intensity
FIG. 11. (Color online) The slice cuts in the H0L plane of the neutron diffraction data from MnBi$_6$Te$_{10}$ collected at 6 K (a) and 18 K (b), respectively, and the difference between these two datasets. There are some notable signal at the magnetic Bragg peak positions from the tails of the nuclear Bragg peaks in the L direction. By taking the difference between 6 K and 18 K, these contribution can be largely removed, and the magnetic Bragg peaks are much visible as seen in (c). Note that panel (c) uses a different color map than (a) and (b).

of magnetic Bragg peak is proportional to the square of the spontaneous staggered magnetic moment; therefore, a factor of 2 is used before the critical exponent in the equation. The magnetic ordering temperatures from the best fits are $13.01 \pm 0.01$ K and $11.53 \pm 0.05$ K for MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$, respectively, which are in a good agreement with their values obtained from the magnetic and transport measurements. The critical exponents are $\beta = 0.39 \pm 0.01$ and $\beta = 0.46 \pm 0.04$ for MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$, respectively, in the studied temperature range.

**Magnetic Structure of MnBi$_4$Te$_7$**

Magnetic structure models are investigated using both the symmetry approach using the MAXMAGN program [18] and the representation analysis with the program SARAh [17] to determine the symmetry-allowed magnetic structures that can result from a second-order magnetic phase transition given the crystal structure and the propagation vector. There are six possible irreducible representations (IRs) associated with the P -3 m 1 space group (#164) and the propagation vector $k = (0 \ 0 \ 0.5)$. The decomposition of the magnetic representation for the Mn $(0 \ 0 \ 0.5)$ site is $\Gamma_{Mag} = \Gamma_2 + \Gamma_6$. The labeling of the IRs follows the scheme used by Kovalev [23]. Table I lists the two non-zero IRs and their associated basis vectors $\psi_i$. $\Gamma_2$ allows ordered magnetic moments along the c-axis and $\Gamma_6$ allows ordered magnetic moments in the ab-plane. Therefore, only $\Gamma_2$ agrees with the observation of absence of magnetic peak along the $[0 \ 0 \ L]$ direction, as discussed above. From the magnetic symmetry approach, there is only one possible maximal magnetic space group, Pc -3c 1 (#165.96), which only allows non-zero ordered magnetic moment along the c-axis, which is consistent with the magnetic structure model based on the repre-

- **TABLE I.** Basis vectors for the space group P -3 m 1 with the magnetic wavevector $k = (0 \ 0 \ 0.5)$ for MnBi$_4$Te$_7$. $\Gamma_2$ allows ordered magnetic moments along the c-axis and $\Gamma_6$ allows ordered magnetic moments in the ab-plane.

| IR BV Atom | BV components |
|------------|---------------|
| $\Gamma_2$ $\psi_1$ Mn | $m_{||a}$ | $m_{||b}$ | $m_{||c}$ | $m_{||b}$ | $m_{||c}$ |
| $\Gamma_6$ $\psi_2$ Mn | 6 | 3 | 0 | 0 | 0 | 0 |
| $\psi_3$ Mn | 0 | -5.196 | 0 | 0 | 0 | 0 |
Magnetic Structure of MnBi$_6$Te$_{10}$

| IR | BV | Atom | $m_{||a}$ | $m_{||b}$ | $m_{||c}$ | $im_{||a}$ | $im_{||b}$ | $im_{||c}$ |
|----|----|------|---------|---------|---------|----------|---------|---------|
| $\Gamma_3$ | $\psi_1$ | Mn | 0 | 12 | 0 | 0 | 0 |
| $\Gamma_5$ | $\psi_2$ | Mn | 0 | -3 | 0 | 0 | 0 | 0 |
| $\psi_3$ | Mn | -3.464 | -1.732 | 0 | 0 | 0 | 0 |

TABLE II. Basis vectors for the space group R -3 m:H with the magnetic wavevector $k = (0 0 1.5)$ for MnBi$_6$Te$_{10}$. $\Gamma_3$ allows ordered magnetic moments along $c$-axis and $\Gamma_5$ allows ordered magnetic moments in the $ab$-plane.

There are six possible irreducible representations (IRs) associated with the R -3 m:H space group ($\#166$) and the propagation vector $k = (0 0 1.5)$. The decomposition of the magnetic representation for the Mn (0 0 0) site is $\Gamma_{Mag} = 1\Gamma_3 + 1\Gamma_5$. Table II lists the two non-zero IRs and their associated basis vectors $\psi_1$. $\Gamma_3$ allows ordered magnetic moments along the $c$-axis and $\Gamma_5$ allows ordered magnetic moments in the $ab$-plane. Therefore, only $\Gamma_3$ agrees with the observation of absence of magnetic peak along the [0 0 L] direction. From the magnetic symmetry approach, there is only one possible maximal magnetic space group, $R_1 -3c$ ($\#167.108$), which only allows non-zero ordered magnetic moment along the $c$-axis, which is consistent with the magnetic structure model based on the representation $\Gamma_3$.

Figure 13(b) shows the magnetic structure model based on the representation $\Gamma_3$ and the refinement results. As mentioned above, there are contributions from the tails from the nuclear Bragg peak at the magnetic peak positions at 6 K. To better separate the nuclear and the magnetic Bragg peaks, the peak integration on the nuclear peaks were conducted using the 18 K dataset; while the peak integration on the magnetic peaks was conducted using the difference between the 6 K and 18 K datasets, where the contribution of the nuclear Bragg peaks have been largely eliminated, as shown in Fig. 11(c). The refined magnitudes of the ordered moments is $3.96 \pm 0.04 \mu_B$ per Mn ion at 6 K. As for the case of MnBi$_4$Te$_7$, the quoted uncertainty only reflects the statistical error. An estimation on the systematic error using different peak integration approaches gives rise to an uncertainty on the order of 0.2 $\mu_B$ per Mn ion.

### DISCUSSION

**Effects of stacking of the septuple and quintuple layers**

Some parameters for all three $n=1, 2$, and 3 members in MnBi$_{2n}$Te$_{3n+1}$ are summarized in Table III. The room temperature $a$ lattice parameter slightly increases with increasing $n$. This suggests that the stacking of the septuple and quintuple layers also modifies the in-plane competing interactions in addition to weakening the interlayer coupling. All three compounds order into an A-type antiferromagnetic structure below $T_N$ in which the magnetic moments within the triangular layers are coupled...
TABLE III. Summary of the properties of MnBi$_{2n}$Te$_{3n+1}$ with n=1, 2, and 3.

| Properties               | MnBi$_{2}$Te$_{4}$ (n=1) | MnBi$_{4}$Te$_{7}$ (n=2) | MnBi$_{6}$Te$_{10}$ (n=3) |
|--------------------------|--------------------------|--------------------------|--------------------------|
| space growth             | R-3m                     | P-3m                     | R-3m                     |
| a (Å)                    | 4.3338(4)                | 4.366                    | 4.374                    |
| c (Å)                    | 40.931(6)                | 23.80                    | 101.93                   |
| T$_N$ (K)                | 24                       | 13                       | 11                       |
| Weiss constant (K)       | 6                        | 11                       | 12                       |
| Effective moment (μB/Mn) | 5.3                      | 5.2                      | 5.0                      |
| Saturation moment (μB/Mn)| 3.56 at 2K               | 3.16 at 2K               | 3.62 at 2K               |
| Ordered moment (μB/Mn)   | 4.04(13) at 10 K         | 3.2(2) at 6 K            | 4.0(2) at 6 K            |
| Interlayer coupling SJc (kOe) | 15.3                  | 1.5                      | 0.53                     |
| Single ion anisotropy (kOe) | 14                    | 17                       | 17                       |
| Field (H//c) effect      | Flop at 33kOe, saturate at 78kOe | Flip at 1.6kOe | Flip at 1.6kOe |
| Field (H//ab) effect     | Saturate at 103kOe       | Saturate at 10kOe        | Saturate at 10kOe        |

Despite the same low temperature magnetic structure, MnBi$_{4}$Te$_{7}$ is different from the other two members with respect to the magnitude of the ordered and the saturation moments. At 6 K, the ordered moment is estimated to be about 3.2(2)μB/Mn for MnBi$_{4}$Te$_{7}$. This ordered moment is slightly larger than the saturation moment of 3.16μB/Mn at 2 K and 70 kOe. MnBi$_{6}$Te$_{10}$ and MnBi$_{2}$Te$_{4}$ have similar ordered moments and comparable saturation moments. Their saturation moments at 2 K are slightly smaller than their ordered moments measured at a higher temperature. At 6 K, the ordered moment is 3.96μB/Mn for MnBi$_{6}$Te$_{10}$. This ordered moment is comparable to 4.04μB/Mn for MnBi$_{2}$Te$_{4}$ measured at 10 K. At 2 K and 70 kOe, MnBi$_{6}$Te$_{10}$ has a saturation moment of 3.62μB/Mn, which is similar to 3.56μB/Mn for MnBi$_{2}$Te$_{4}$. The difference between MnBi$_{4}$Te$_{7}$ and the other two members might be rooted in the stacking of the magnetic layers in these three compounds. If we look at the stacking of the magnetic septuple layers, MnBi$_{2}$Te$_{4}$ and MnBi$_{6}$Te$_{10}$ show the same ABC-type stacking of the magnetic layers (see Figs. [10][13]).

The stacking of the septuple and quintuple layers along the c-axis has a dramatic effect on the magnetic properties in an applied magnetic field. In magnetic fields applied along the crystallographic c-axis, the magnetic moments in MnBi$_{2}$Te$_{4}$ flop to an alignment perpendicular to the field above about 35 kOe and then gradually rotate to parallel alignment above 78 kOe. In contrast, the magnetic moments in MnBi$_{4}$Te$_{7}$ and MnBi$_{6}$Te$_{10}$ never become perpendicular to the applied field, but flip to be parallel to the field direction in a small critical field of about 1.6 kOe. The latter field dependence is similar to that for MnSb$_{2}$Te$_{4}$ where SJc/SD is smaller than 2/z required for the spin flop transition. With the magnetic septuple layers further separated by the nonmagnetic quintuple layers in MnBi$_{4}$Te$_{7}$ and MnBi$_{6}$Te$_{10}$, the interlayer coupling SJc is reduced while the single ion anisotropy SD is less affected.

As for the case of MnSb$_{2}$Te$_{4}$, the interlayer antiferromagnetic exchange (Jc) and single-ion anisotropy (D) can be estimated from the critical magnetic field H$_{c}$ for the spin flip transition and the critical field H$_{s}$ applied perpendicular to the c-axis to saturate the magnetic moment: SJc=gμ$_{B}$H$_{c}$/z, SD=(1/2)gμ$_{B}$H$_{s}$-zSJc, where g=2, z is the coordination number for Mn to other Mn in layers above and below. It is worth mentioning that z=2 for MnBi$_{4}$Te$_{7}$ and z=6 for MnBi$_{6}$Te$_{10}$. As expected, SJc=1.5 kOe of MnBi$_{4}$Te$_{7}$ is about three times of SJc=0.53 kOe for MnBi$_{6}$Te$_{10}$; SD is comparable to each other for these two compounds. It should be noted that SD is also comparable to those in MnSb$_{2}$Te$_{4}$ and MnBi$_{2}$Te$_{4}$. These parameters are listed in Table III. The ratio of SJc/SD is 0.2 and 0.08 for MnBi$_{4}$Te$_{7}$ and MnBi$_{6}$Te$_{10}$, respectively. Both are smaller than 1/3 required for the occurrence of a spin flop transition. The spin gap estimated as ∆=2SD√zSJc/SD+I is around 37 kOe for both compounds.

The above estimation suggests that the separation of the magnetic septuple layers by the nonmagnetic quintuple layers in MnBi$_{2n}$Te$_{3n+1}$ with increasing n significantly reduces the interlayer coupling SJc. However, the experimentally observed A-type antiferromagnetic order at T>10 K indicates an important role of SJc in determining the magnetic structure. In MnBi$_{6}$Te$_{10}$ with n=3, SJc, although only about 8% of SD, seems to be enough to stabilize the A-type magnetic order. However, with further increasing the number of the nonmagnetic quintuple layers in between the magnetic septuple layers, we would expect that a long range ferromagnetic order is stabilized by SD [22]. It would be interesting to synthesize and check the magnetic properties of MnBi$_{2n}$Te$_{3n+1}$ with n≥4. The persistence of magnetism in MnBi$_{2n}$Te$_{3n+1}$ series will be further discussed later.

Despite the dramatic effect of the stacking of the septuple and quintuple layers on the magnetic properties,
all three compounds show similar temperature dependence of transport properties. Cooling across $T_N$, the in-plane electrical resistivity shows a cusp-like feature; the in-plane thermal conductivity shows a dip-like feature typical of critical scattering; and thermopower shows no detectable anomaly. The dip-like feature induced by the critical scattering is less pronounced in MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$ as shown in (7b). This might result from the dilute effect by the nonmagnetic quintuple layers. This dilution effect can also contribute to the weaker lambda-type anomalies in specific heat (see Fig. 5) with increasing $n$.

The stacking of the septuple and the quintuple layers along the crystallographic $c$-axis can also affect the topological properties in MnBi$_{2n}$Te$_{3n+1}$ compounds. In MnBi$_2$Te$_4$, the termination surface is always the septuple layers and recent photoemission studies reported gapless Dirac surface states [25–28]. In MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$, the termination surface can be the septuple layers or the quintuple layers. Recently photoemission studies on MnBi$_3$Te$_7$ reported gapped (001) surface states when the termination surface is the septuple layer; when the termination layer is the quintuple layer, the upper Dirac cone goes deeper down in energy and merges with the bulk valence band. [10] [11] While the origin and observation of the gapless Dirac surface states in MnBi$_2$Te$_4$ are still under debate, it has been proposed that the surface septuple layer might show a different magnetic order than the bulk. In MnBi$_4$Te$_7$, the quintuple layer beneath the termination septuple layer can help isolate the termination septuple layer from the bulk. In the case that the termination layer is the nonmagnetic quintuple layer, it can behave as a capping layer and reduce the relaxation or reconstruction of the magnetic septuple layer. From this point of view, it would be interesting to check the band structure of MnBi$_6$Te$_{10}$ with the two layers of the quintuple layers on top of the septuple layer.

**Persistence of magnetism**

It is interesting to notice the persistence of the magnetism, both in terms of ordered Mn moments of order 4 $\mu_B$, as well as significant Neel points above 10 K, even as the $c$-axis distance between interlayers of Mn approaches dozens of Angstroms in, for example MnBi$_6$Te$_{10}$. Given the general exponential fall-off (at large distances) of atomic-level wavefunctions such as those relevant for Mn (local) magnetism, should not the interlayer exchange coupling rapidly fall to zero as the number of intervening Bi$_3$Te$_3$ layers increases, thereby driving the Neel point to zero, along with the ordered moment? It is a priori rather surprising for a material, such as MnBi$_6$Te$_{10}$, in which only one of 17 atoms is a characteristically magnetic atom, to exhibit a significant magnetism as found here.

In order to understand the persistence of magnetism in MnBi$_{2n}$Te$_{3n+1}$ with $n \geq 2$, we have performed first principles calculations. Our first principles calculations, along with the previous Monte Carlo theoretical work of Yasuda et al. [29], provide a partial answer to this question. For each of the three compounds MnBi$_2$Te$_4$, MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$, we have used the augmented plane-wave density functional theory code WIEN2K [30], employing the generalized gradient approximation of Perdew, Burke and Ernzerhof [31]. We have used a value of 8.0 for RK$_{\text{max}}$, in general the product of the smallest muffin-tin radius and the largest plane-wave expansion wavevector. For all calculations and all atoms a muffin-tin radius of 2.5 Bohr was used. Experimental lattice parameters were used, with internal coordinates optimized in a ferromagnetic configuration, as substantial recent work [32] [33] in this area has found strong magnetoelastic coupling in these materials. Spin-orbit coupling was not included.

For the first two materials we have also calculated the interlayer magnetic coupling, which is defined here as simply the energy difference, per Mn, between the ferromagnetic state and a state with neighboring Mn planes anti-aligned. For the third material this last calculation did not yield reliable results (possibly related to the highly anisotropic crystal structure) and we will therefore discuss the interlayer coupling here in terms of the experimental results. In any case the interlayer coupling for MnBi$_6$Te$_{10}$ is likely sufficiently small as to be near the accuracy of the calculation, given the Mn-Mn interlayer distance here of over 30 Å, so it is sensible to discuss this based on the experimental results.

For all materials here our calculations find the Mn to be in a high-spin ($S = 5/2$) state, as for all three materials, the ordered ferromagnetic moment (per Mn) is 5.0\(\mu_B\). The ordered moment in the experimentally observed A-type (antiferromagnetic ground state, is slightly smaller, at 4.29 \(\mu_B\) for MnBi$_2$Te$_4$ and MnBi$_4$Te$_7$, but this value is only within the muffin-tin spheres (there is a similar muffin-tin-only value for the ferromagnetic state). For these two materials this ground state has insulating character, with respective band gaps of 0.63 and 0.45 eV. These band gaps may be understated relative to actual values given the usual GGA underestimation of band gaps. We believe that the smaller experimentally observed ordered moment may be due to the presence of some disorder in the sample, given the partial occupancies that several structural refinements in the literature find in this family of materials.

The calculated interlayer coupling, as discussed above, is 3 meV/Mn for MnBi$_2$Te$_4$ and 0.5 meV for MnBi$_4$Te$_7$. This 6:1 ratio is in reasonable accord, considering the disorder, with the ratio of nearly 10:1 derived from magnetic data (See Table III). Following the results listed in Table III, we will simply assume that the interlayer coupling for the MnBi$_6$Te$_{10}$ compound is 1/3 of the calculated value.
for the MnBi$_4$Te$_7$ compound, or 0.17 meV/Mn. This is less than 2 K and is substantially smaller than the 11 K ordering point. In the simplest isotropic approximation (clearly inapplicable here), ordering points are estimated as a third of these energy differences, or less than 1 K. How can all these materials then exhibit ordering points much larger than these values?

We provide a possible explanation for this behavior in terms of previous Monte Carlo work on quasi-two dimensional Heisenberg antiferromagnets [29], which focused specifically on the effects on the Neel point $T_N$ of the ratio of exchange constants $J'/J$, where in this case $J'$ would be the interlayer exchange constant and $J$ the planar exchange constant. Note that that theoretical work assumed a simple cubic lattice, while here we have highly anisotropic hexagonal and rhombohedral crystal structures, so that we cannot claim exact applicability of these results here. Nevertheless, the basic physics of anisotropic magnetism is likely to be similar. This is bolstered by the fact that the antiferromagnetic geometric frustration (relevant to hexagonal or rhombohedral materials as considered here) that could confound such an analogy is not operative as all Mn atoms in a given plane are ferromagnetically aligned.

The most relevant finding from that work is that for small values $J'/J < 1$, the Neel point follows the approximate relationship $T_N \sim -1/\ln(J'/J)$. Now, this is in fact a very weak relationship for small $J'$; in particular if the ratio $J'/J$ is allowed to vary from 0.1 to 0.01, the corresponding ratios of Neel points would be approximately 1:1/2:1/3. Thus a hundred-fold reduction in interlayer exchange coupling only reduces the ordering point by an approximate factor of 3. This is again broadly consistent with our experimental finding that a thirty-fold reduction in interlayer coupling (from MnBi$_2$Te$_4$ to MnBi$_6$Te$_{10}$) only reduces the ordering point by roughly a factor of 2.

Finally, we briefly discuss the theoretical finding that the ordered moment is 5.0 $\mu_B$ for all three materials. This is the expected value for divalent Mn in an insulating material, and mainly reflects the local physics of moment formation, as opposed to the ordering point, which derives from interatomic exchange interactions. These interactions, for the interlayer coupling, must necessarily involve numerous intervening atoms. Yet in all these structures, there are 6 Te nearest-neighbor atoms to Mn, just as in MnTe itself, which is also an $S = 5/2$ material. Hence a picture emerges in which the main function of the intervening Bi$_2$Te$_3$ layers is to reduce the interlayer exchange coupling and thereby the Neel point, though we have argued that the fall-off of Neel point with this coupling is rather weak. Since compounds with even more intervening Bi$_2$Te$_3$ layers are possible [4], the argument presented suggests that these too may have significant ordering points. It will therefore be of substantial interest to synthesize and characterize these compounds.

**SUMMARY**

In summary, we study the A-type antiferromagnetic order in MnBi$_4$Te$_7$ and MnBi$_6$Te$_{10}$ single crystals by measuring the magnetic, transport, and thermodynamic properties as well as neutron single crystal diffraction. The comparison with MnBi$_4$Te$_4$ suggests that the stacking of the magnetic septuple layers and increased spacing between them have dramatic effect on the magnetic properties. The nonmagnetic quintuple layers in between the magnetic septuple layers significantly reduce the magnitude of interlayer coupling. However, single ion anisotropy shows little change with increasing n in MnBi$_{2n}$Te$_{3n+1}$ compounds. This suggests that the septuple layers are similar in all these compounds. This also indicates that a long range ferromagnetic order is expected when further increasing the spacing between the septuple layers.

We noticed that the saturation moment at 2K from magnetic measurement is slightly smaller than the ordered moment measured by neutron scattering at a higher temperature for both MnBi$_2$Te$_4$ and MnBi$_6$Te$_{10}$. We would expect the difference could be even larger if the ordered moment at 2K was used for comparison. The fact that the saturation moment is smaller than the ordered moment is unusual. The magnetic structure of these compounds at low temperatures deserve further careful study especially in the presence of high magnetic fields. The small critical magnetic fields required for spin flip (H//c) and moment saturation (H//ab) facilitate the measurements in most four-circle instruments.

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