Phonon modes and Raman signatures of $MnBi_{2n}Te_{3n+1}$ (n = 1, 2, 3, 4) magnetic topological heterostructures

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An intrinsic antiferromagnetic topological insulator $MnBi_2Te_4$ arises when intercalating a Mn-Te bilayer chain in a topological insulator, Bi_2Te_3 . We present observations on the inter- and intralayer phonon modes of the generalized Mn $Bi_{2n}Te_{3n+1}$ (n = 1, 2, 3, 4) family using cryogenic low-frequency Raman spectroscopy with various polarization configurations. Two peaks at 66 and 112 cm⁻¹ show abnormal perturbation in Raman linewidths below magnetic transition temperature due to spin-phonon coupling. In MnBi₄Te₇, Bi₂Te₃ layers induce Davydov splitting of the A_{1g} mode around 137 cm⁻¹ at 5 K. The out-of-plane interlayer force constant estimated using the linear chain model was (3.98 ± 0.14) × 10^{19} N/m³, three times weaker than that of Bi₂Te₃. Adding more Bi₂Te₃ layers, such as MnBi₆Te₁₀ and MnBi₈Te₁₃, makes Bi₂Te₃ properties more dominant than magnetic properties. Our work experimentally and theoretically discovers the dynamics of phonon modes of Mn Bi_{2n}Te_{3n+1} family, facilitating utilization of magnetic topological heterostructures.

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The remarkable potentials of magnetic topological insulators, realizing exotic physical phenomena [1-3] like quantum anomalous Hall effect [4–7] or axion insulators [8–10], have led researchers striving to combine topological properties and magnetism by creating a proximity effect between a topological insulator and magnetic material [11], or by chemical doping [7,12,13]. However, synthesizing the material uniformly over a large area with well-controlled doping concentration has proven difficult. The recent discovery of intrinsic antiferromagnetic topological insulator MnBi₂Te₄ overcomes these difficulties [4,8,14,15]. It can be synthesized into a few millimeters of uniform bulk single crystals and its layered structure exhibits interesting thickness dependence [16]. For example, a structure with an odd number of MnBi₂Te₄ layers is ferromagnetic, while that with an even number of layers (or bulk) becomes antiferromagnetic due to its head-to-head spin alignment [16-20]. Furthermore, inserting Bi₂Te₃ layers between two adjacent MnBi₂Te₄ layers changes the interlayer interactions, leading to altered physical properties such as different magnetic properties [15,17,18,21–24]. For example, the Néel temperature (T_N) of bulk MnBi₂Te₄ is 25 K [19,20], for MnBi₄Te₇ is 13 K [17,22,23] and for MnBi₆Te₁₀ is 11 K [23,24]. Contrastingly, MnBi₈Te₁₃ becomes ferromagnetic below 10.5 K [21]. Their bulk properties have been studied by various methods, including transport measurements [19,21–24], angle-resolved photoemission spectroscopy [17,20–22,25,26], x-ray scattering [19,23], and magnetic susceptibility measurements [17,19,22,23].

Here we present the study of phonon vibrational modes in the generalized Mn $Bi_{2n}Te_{3n+1}$ (MBT, n = 1, 2, 3, 4) family using linearly and circularly polarized cryogenic lowfrequency optical Raman spectroscopy, supported by firstprinciples density functional theory (DFT) calculations. Raman spectroscopy is nondestructive and highly sensitive to small changes in the lattice dynamics and magnetic ordering down to the two-dimensional limit [19,27–33]. This work provides a thorough examination and physical understanding of intralayer phonon dynamics in the Mn $Bi_{2n}Te_{3n+1}(n = 1, 2, 3, 4)$ family and interlayer interactions, in support of magnetic topological insulator studies at the few-layers limit.

Figure 1(a), left panel, depicts the side view of the $MnBi_2Te_4$ crystal structure. One unit layer consists of seven atomic layers (a septuple layer) and is a compound of a Bi_2Te_3 and a Mn-Te bilayer chain, of which the latter is shown in the dashed box. The top view of $MnBi_2Te_4$ has threefold symmetry as illustrated in the middle panel of Fig. 1(a) [15]. We synthesize Mn $Bi_{2n}Te_{3n+1}$ (n = 1, 2, 3, 4) single crystals with Bi_2Te_3 flux [21,22,25,26,34]. Mn, Bi, and Te elements,

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FIG. 1. Polarized optical Raman spectroscopy of magnetic topological insulators, distinguishing *E*-mode and *A*-mode phonons. (a) Crystal structure of MnBi₂Te₄ (left), top view of MnBi₂Te₄ (middle), and exemplary optical image of samples (right). Scale bar: 20 μ m. (b) The figure shows the layered structure of MBT families. (c) shows Raman spectrum (top) of MnBi₂Te₄ in the *E* mode (red) and *A* mode (blue), measured at 7 K. DFT calculation (bottom) shows corresponding Raman peak positions in each polarization configuration. The grey shaded area below 30 cm⁻¹ indicates the cut-off filter frequency. (d) Linear parallel polarization dependence of Raman signal at 7 K.

at a molar ratio of 15:170:270, are loaded in a crucible and sealed in a quartz tube under one-third atmospheric pressure of Ar. The ampule is heated to 900 °C for 5 h, followed by air-quenching. It is then transferred to another furnace to cool it slowly from 595 °C to the decanting temperature, which varies for different *n* [21]. After resting the samples for one day, we centrifuge the ampule to separate the Mn Bi_{2n}Te_{3n+1} crystals from the flux. To achieve clean and flat surfaces for the optical measurements, we mechanically exfoliate the bulk single crystals on Si substrates, with an example illustrated in Fig. 1(a), right panel. The average thickness of the flakes is bigger than 100 nm. All crystallographic structure images were produced by VESTA [35].

The layered structures of MBT families are shown in Fig. 1(b), which are equivalent to heterostructures with a $MnBi_2Te_4$ and a differing number of Bi_2Te_3 . For example, $MnBi_4Te_7$, $MnBi_6Te_{10}$, and $MnBi_8Te_{13}$ have one, two, and three Bi_2Te_3 layers between two $MnBi_2Te_4$ layers, respectively. For the Raman measurements, we use a 532.2-nm laser, with an 80× objective lens at a power below 1 mW. Two Ondax notch filters suppress the Rayleigh scattering and reveal low-frequency Raman peaks down to 30 cm⁻¹. The Raman

spectrum is acquired with a Horiba 1000 M spectrometer with 1200 grooves/mm grating and the spectrometer was calibrated with a Mercury lamp and Si Raman peak at 520 cm⁻¹ before the measurements. To ensure the repeatability of the Raman signal, we probe several flakes, whose spectra are consistent within the experimental uncertainties. No laser-induced degradation of Raman peak intensities is observed over a few hours.

Figure 1(c) shows an example Raman spectrum of a bulk MnBi₂Te₄ at 7 K (top) and the calculated peak positions from the DFT (bottom). According to group theory, the crystal structure of bulk MnBi₂Te₄ belongs to the space group $R\bar{3}m$ (No. 166, point group D_{3d}) [34,36,37], and it has doubly degenerate E_g and nondegenerate A_{1g} symmetry Raman modes. To experimentally verify the E and A modes of the Raman peaks, we use circular polarization, the description of which can be found in Fig. S1 in the Supplemental Material (SM) [38]. From the Raman tensor analysis provided in the SM [38,39], E modes only appear in $\bar{z}(\sigma^- - \sigma^+)z$ configuration, while A modes are only present in $\bar{z}(\sigma^- - \sigma^-)z$ configuration. From our measurements, we assign Peaks II and III to E modes (red) and Peaks I, IV, and V to A modes (blue), consistent with DFT calculations where red (blue) lines are E (A) modes. The gray shaded area indicates the cutoff frequency in the polarized cryogenic Raman setup. The lowest frequency of the *E* modes of 30.3 cm^{-1} from theory was measured with Horiba T64000 Raman spectrometer in ambient, shown in Figure S2 in the SM. In Fig. 1(d), we present the incident linear polarization dependence of MnBi₂Te₄ at 7 K, maintaining the relative angle of the analyzer in the parallel polarization configuration. The polarization dependence remains isotropic, consistent with our theoretical analysis for the $R\bar{3}m$ space group without considering the spin ordering (more details in the SM, Sec. 3). This means that in-plane magnetic anisotropy from spin-phonon coupling is not observed in the antiferromagnetic state. Vibrational modes and the temperature dependence of MnBi₂Te₄ Raman spectrum are discussed in depth later.

Figure 2 presents the Raman spectra of Mn Bi_{2n} Te_{3n+1} (n = 1, 2, 3, 4) at room temperature. Each sample has (n-1) number of Bi₂Te₃ layers between two MnBi₂Te₄ layers. In all samples, we observe four distinctive peaks around 42 (peak I), 60 (II), 100 (III), and 135 $\rm cm^{-1}$ (V), and a shoulder peak around 110 cm⁻¹ (IV). The peak marked with * comes from the laser. As *n* increases, the peak positions and the widths converge to those of Bi₂Te₃; light horizontal lines in Figs. 2(c)-2(d). Compared to the Raman spectrum of Bi₂Te₃, Peaks I, II, and IV uniquely exist in MnBi₂Te₄. Our DFT calculations show that the Mn atom of the Mn-Te bilayer chain remains static in all vibrational modes, while the Te atom oscillates in- or out-of-plane in Peaks I, II, and IV; see the inset in Fig. 2(b) for peak III as an example and all the vibrational modes in Fig. S3a in the SM. When $n \ge 2$, the additional Bi₂Te₃ layer either introduces a new peak or shifts the existing peaks (Fig. S3b in the SM). For example, the main contribution to the E_{g} mode of Peak III in MnBi₂Te₄ comes from the vibrations of the top and the bottom Bi-Te atomic layers, similar to that of Bi₂Te₃. Therefore, the additional Bi2Te3 layer simply shifts the peak position, instead of creating a new mode.



FIG. 2. Effects of Bi₂Te₃ intercalation on Raman spectra of Mn Bi_{2n}Te_{3n+1} topological heterostructures. (a), (b) Raman spectra measured at room temperature in linear polarization configuration without an analyzer and with circularly polarized light $[\bar{z}(\sigma^{-} - \sigma^{+})z]$, respectively. Inset shows example of in-plane vibration of structure corresponding to peak III. (c), (d) Evolution of Raman peaks positions and widths, respectively. Light horizontal lines indicate peak positions and widths of bulk Bi₂Te₃ measured at the same temperature.

In Peak II, the Bi₂Te₃ layer generates a new peak when it oscillates out-of-plane (A_{1g}) while the MnBi₂Te₄ layer remains almost static (calculated frequency of 58.8 cm⁻¹ in Fig. S3b, SM). This peak position overlaps with the E_g vibration of MnBi₂Te₄ where the Bi₂Te₃ layer stays static (calculated frequency of 68.9 cm⁻¹ in Fig. S3b, SM). Therefore, Peak II with E_g symmetry in the pure MnBi₂Te₄ bulk develops into two mixed peaks in the MnBi₂Te₄/Bi₂Te₃ heterostructure, i.e., one peak still with E_g symmetry with the vibrating MnBi₂Te₄ layer, and the other one with A_{1g} symmetry with the vibrating Bi₂Te₃ layer.

We use a circular polarization configuration to experimentally confirm the symmetries. In Fig. 2(b), the spectrum, measured in $\sigma^- - \sigma^+$ circular polarization, shows only the *E* modes. We observe that Peak II in MnBi₂Te₄ redshifts with increasing *n*. The decreased intensity is due to the reduced number of vibration entities in the unit area, owing to the static Bi₂Te₃ layers in the vibration patterns of Peak II. The dominating intensity around 60 cm⁻¹ above n = 2 in Fig. 2(a) is from the A_{1g} mode of Bi₂Te₃, which is absent in MnBi₂Te₄, as expected from our theory. Polarization measurements in the parallel, cross, and $\sigma^- - \sigma^-$ polarization configurations are shown in Fig. S4 in the SM, to further differentiate these two mixed peaks. The evolution of the peak positions and the widths with *n* is presented in Figs. 2(c) and 2(d), respectively. The exact Raman peak positions from the experiment and the theory are given in the Table S1, SM. To observe the evolution of the peak II (orange dashed line), we fit the E_g mode with Lorentzian in Fig. 2(b), where the A_{1g} mode from the Bi₂Te₃ layer is suppressed. The orange solid line represents the A_{1g} mode from the Bi₂Te₃. As expected, the peaks get closer to that of Bi₂Te₃ with increasing *n*. In this measurement, we observe a Davydov splitting of Peak V on MnBi₄Te₇ (blue dashed line, n = 2), which will be discussed further in Fig. 4.

To understand the effect of magnetic ordering on Raman spectrum of MnBi₂Te₄, we examine the temperaturedependent spectra from 294 to 5 K. Figure 3(a) shows no new peaks below the Néel temperature, indicating that the magnetic ordering does not significantly change the vibrational modes. Figure 3(b) displays the Raman peak shifts of Peak II(E_g^2), IV(A_{1g}^2) and V(A_{1g}^3), relative to those at room temperature. The rest can be found in the SM, Fig. S5. The peak shifts follow the general temperature-dependent anharmonicity model based on phonon decays into different number of phonons [40], i.e., monotonic blueshift down to \approx 40 K, followed by almost constant peak positions at lower temperatures. This model describes our experimental data well, represented by solid lines. In the same model, we would expect the widths of the Raman peaks to get narrower at lower temperatures, as observed in Peaks I, III, and V [e.g., Fig. 3(d) for Peak V and Fig. S5 in the SM for Peaks I and III] [40]. Interestingly, we find that Peaks II and IV behave differently. Peak IV widens by $\approx 20\%$ at low temperatures, as in Fig. 3(d), green scatter points. Peak II becomes broader below 20 K, while the width barely changes above 20 K, as in Fig. 3(e). The abnormal change of Peak II and IV is also demonstrated in thin samples. On 10-nm thickness MnBi₂Te₄ flake, the width of the Peak IV widens by $\sim 16\%$ at 7 K and Peak II remains unchanged within experimental uncertainties, as opposed to other peaks that become more than 20% narrower, as shown in Fig. S6 in the SM. This abnormal behavior is discordant with the anharmonicity model. For Peaks I, III, and V, the main contribution comes from the vibrations of the top and the bottom Bi-Te chains, not directly bonded to Mn atoms [Fig. 3(c), right panel, and Fig. S3a]. Conversely, the main contribution to Peaks II and IV comes from the vibrations of the Te atoms that are directly neighboring with Mn atoms [left two panels in Fig. 3(c)]. Therefore, below the T_N , the spin-phonon coupling would be more pronounced in Peaks II and IV, matching our measurements. We further confirmed the AFM ordering with DC magnetic susceptibility measurement, as shown in Fig. 3(e), right axis. The magnetic susceptibility peaks at 23.3 K, which is a signature of AFM. We do not expect the order-parameter-like temperature dependence here, because the net magnetization is close to zero in the ordered AFM phase. Hence, we attribute the observed broadening of the peaks, and therefore decreased phonon lifetime, to the spin-phonon coupling [27,41,42]. The temperature from which the Raman peak broadens is slightly lower than the T_N . This is because the change in the width is too small near the T_N



FIG. 3. Temperature dependences and intralayer spin-phonon coupling of antiferromagnetic $MnBi_2Te_4$ topological insulator. (a) Raman spectra measured in temperatures ranging from 5 to 294 K. Peaks marked with * are from laser. (b) Change in Raman peak positions of $II(E_g^2)$, $IV(A_{1g}^2)$ and $V(A_{1g}^3)$, relative to those measured at room temperature. Solid lines represent fitting based on anharmonicity model. (c) Vibrational patterns of the II, IV, and V modes. (d) Widths of peak $V(A_{1g}^3)$ and peak $IV(A_{1g}^2)$, obtained from Lorentzian fits. Blue solid line is fit with anharmonicity model. (e) Temperature dependent Raman linewidth of Peak II (red scatter points, left axis) and magnetic susceptibility of bulk $MnBi_2Te_4$ (black solid line, right axis). The shaded area in (b), (c), and (e) indicates the experimental errors.

and falls within the experimental uncertainties. In MnBi₄Te₇, we also observed a broader width of Peak IV (Fig. S7 in the SM), but could not isolate the E_g mode from the MnBi₂Te₄ vibration due to dominating A_{1g} mode from the Bi₂Te₃ layer near the same frequency.

When a Bi2Te3 layer forms a heterostructure with MnBi₂Te₄, it not only introduces an additional mode from Bi_2Te_3 , e.g. A_{1g} mode at 60 cm⁻¹, but also perturbs an intralayer vibration mode in bulk MnBi₂Te₄ and splits a peak, known as Davydov splitting [43], as presented in Fig. 4. This Davydov splitting has been observed in other layered materials, such as $MoSe_2$ [44] and $MoTe_2$ [45]. Figure 4(a) shows the zoomed-in temperature-dependent spectra near Peak V, 135 cm^{-1} . The full spectrum can be found in the SM, Fig. S7. At room temperature, the large linewidths make the splitting less distinct. The narrower linewidths at cryogenic temperatures reveal Davydov splitting and the shoulder clearly. Figure 4(b) summarizes the central frequencies of the split from the two Lorentzian fits [purple and green in Fig. 4(a)] at 136.6 and 140.2 cm^{-1} at 5 K. The $\approx 4 \text{ cm}^{-1}$ peak separation slightly widens at room temperature (132.0 and 136.3 cm⁻¹), as can be seen on the right axis (grey scatter points) in Fig. 4(b).

From our calculations, the A_{1g} mode of MnBi₂Te₄ at 144.1 cm⁻¹ (138.6 cm⁻¹ peak in the experiment) has its Raman-inactive Davydov pair at 146.0 cm⁻¹. In MnBi₄Te₇,

the additional Bi2Te3 has a similar, but not identical, vibration pattern to the A_{2u} mode in MnBi₂Te₄. The symmetry breaking by the additional Bi₂Te₃ layer renders this mode Raman active in MnBi₄Te₇ and induces the A_{1g} peak at 143.4 cm⁻¹ [see Fig. 4(c)]. The A_{1g} mode of MnBi₂Te₄ at 144.1 cm⁻¹ then downshifts to 141.3 cm⁻¹ in MnBi₄Te₇. Therefore, a single A_{1g} peak in MnBi₂Te₄ appears as two A_{1g} peaks in the Raman spectrum of MnBi₄Te₇, corroborating our experimental observations. In the A_1 -like vibrational mode, the vibrational frequencies of these two peaks are related as $\omega_1^2 =$ $\omega_0^2 + \omega_{\rm LB}^2$ where ω_0 is the original A_{1g} peak (136.6 cm⁻¹; experiment at 5 K) and ω_1 is its Davydov pair (140.2 cm⁻¹; experiment at 5 K) [46,47]. ω_{LB} is the frequency of layer breathing (LB) mode. From this expression, we experimentally find that ω_{LB} is $31.7 \pm 0.6 \text{ cm}^{-1}$ at 5 K and $33.7 \pm 2.5 \text{ cm}^{-1}$ at 297 K. Theoretically, we estimate the ω_{LB} (A_{2u}) mode; Raman inactive) to be 22.48 cm⁻¹ which deviates from our measurements due to the overestimated peaks from the DFT calculations. Using the linear chain model [45,46,48], we can estimate the out-of-plane interlayer force constant (K^{\perp}) using $\omega_{\rm LB} = (1/\pi c) \sqrt{K^{\perp}/\mu}$; c is the speed of light and μ is the effective mass per unit area. The estimated interlayer K^{\perp} in MnBi₄Te₇ thus ranges from $(3.98 \pm 0.14) \times 10^{19}$ N/m³ to $(4.48 \pm 0.66) \times 10^{19} \text{ N/m}^3$ between 5 K and room temperature, which is about a third of the value in Bi_2Te_3 [46]. In MnBi₆Te₁₀ and MnBi₈Te₁₃, it is difficult to observe such



FIG. 4. Intralayer Davydov splitting from interlayer interactions in $MnBi_4Te_7$ heterostructures. (a) Temperature dependences of $MnBi_4Te_7$, focusing on Peak V centered at 135 cm⁻¹. Two Lorentzian fits for Peak V are shown for spectrum at 5 K. (b) Evolution of the splitting Raman peaks (left axis; green and purple) and the peak separation between the Davydov pair (right axis; grey). (c) Change in vibrational modes between $MnBi_2Te_4$ and $MnBi_4Te_7$ (MnBi₂Te₄/Bi₂Te₃ heterostructure) based on DFT calculations.

a splitting at this excitation wavelength because dominating Bi_2Te_3 vibrational modes obscure the Davydov splitting.

In summary, we examined the phonon dynamics of the layered $Mn Bi_{2n}Te_{3n+1}$ magnetic topological insulator using polarized low-frequency Raman spectroscopy at cryogenic temperatures supported by first-principles DFT calculations of the phonon modes. Comparison of $MnBi_2Te_4$ and $MnBi_4Te_7$ provides us the best contrast in the Raman phonon spectra due to a newly introduced Bi_2Te_3 layer. From $MnBi_4Te_7$ to $MnBi_8Te_{13}$, the phonon spectrum changes more gradually. In $MnBi_2Te_4$, the anomalous broadening of the 66 cm⁻¹ peak is observed below the Néel temperature, the origin of which is explained by the intralayer spin-phonon coupling. When a Bi_2Te_3 layer is inserted between two $MnBi_2Te_4$ layers, an out-of-plane vibrational mode from Bi_2Te_3 dominates Peak II. We also observed and quantified the Davydov splitting of

 A_{1g} mode at 136.6 cm⁻¹, arising from interlayer interactions between Bi₂Te₃ and MnBi₂Te₄. The estimated out-of-plane interlayer force constant is between (3.98 ± 0.14) to (4.48 ± 0.66) × 10¹⁹ N/m³, at 5 and 294 K, respectively, which is weaker than that of Bi₂Te₃ by a factor of 3. Our studies deepen the understanding of the phonon modes and layer interactions in the Mn Bi_{2n}Te_{3n+1} magnetic topological insulator family, including circularly polarized excitations, anharmonic shifts and broadening, spin-phonon coupling, and Davydov splitting. It unveils the role of the intercalated Mn-Te bilayers in Bi₂Te₃ and supports the control of the physical processes in heterogeneous magnetic topological insulators.

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Y. C. designed and led the study of the Raman experiment on Mn Bi_{2n}Te_{3n+1}(n = 1, 2, 3, 4) including the measurements at low temperatures and building the low-frequency Raman setup. J.H.K. and M.T. performed the Raman experiments and obtained optical images. Y.C, J.H.K., and C.W.W. analyzed the experimental data. A.A.P., Y.C., S.G., F.K., A.A.B. measured preliminary Raman spectra at Oak Ridge National Laboratory (A.A.P. and Y.C.) and University of California, Riverside (S.G., F.K., A.A.B.). L.L., X. K. performed the DFT calculations to support the experimental Raman data. C.H. and N.N. provided the bulk single crystals used in this study. Y.C., J.H.K., L.L., A.A.P. and C.W.W. prepared the manuscripts. C.W.W. led and supported this research. All authors discussed the results.

The authors declare no competing interests.

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