

Observation of Ultrastrong Coupling between Substrate and the Magnetic Topological Insulator MnBi_2Te_4

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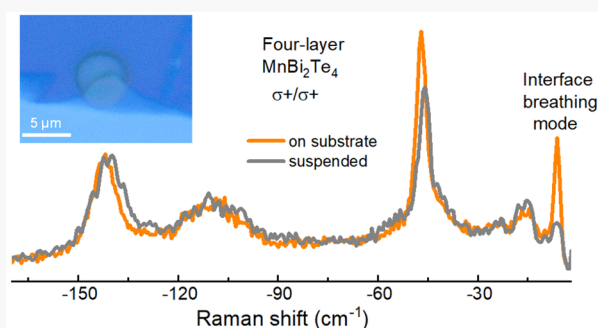
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Supporting Information

ABSTRACT: The intrinsic magnetic topological insulator MnBi_2Te_4 has attracted significant interest recently as a promising platform for exploring exotic quantum phenomena. Here we report that, when atomically thin MnBi_2Te_4 is deposited on a substrate such as silicon oxide or gold, there is a very strong mechanical coupling between the atomic layer and the supporting substrate. This is manifested as an intense low-frequency breathing Raman mode that is present even for monolayer MnBi_2Te_4 . Interestingly, this coupling turns out to be stronger than the interlayer coupling between the MnBi_2Te_4 atomic layers. We further found that these low-energy breathing modes are highly sensitive to sample degradation, and they become drastically weaker upon ambient air exposure. This is in contrast to the higher energy optical phonon modes which are much more robust, suggesting that the low-energy Raman modes found here can be an effective indicator of sample quality.

KEYWORDS: MnBi_2Te_4 , Raman spectroscopy, layer dependence, breathing modes, linear chain model



The quest for interplay between magnetism and topological order has led to the discovery of MnBi_2Te_4 (MBT), a layered ternary chalcogenide¹ predicted to host versatile nontrivial topological phases.^{2–7} An individual MBT layer is seven atoms thick, arranged in the order of Te–Bi–Te–Mn–Te–Bi–Te as illustrated in Figure 1a. Within each septuple layer (SL) of MBT, the Mn ions in the central plane couple to each other ferromagnetically (FM) with an out-of-plane easy axis. Between two neighboring MBT SLs, interlayer exchange interactions between Mn planes are antiferromagnetic (AFM), giving rise to an A-type AFM material system with zero net magnetization at low temperatures.^{8–10} Due to a large spin–orbit interaction that causes band inversion and protection from a symmetry composed of time reversal and a half-lattice-constant translation along the *c* axis, MBT realizes a widely sought after intrinsic magnetic topological insulator. Recent charge transport studies of few-layer MBT indeed showed encouraging signatures of nontrivial topology that are highly sensitive to device layer number.^{11–15} Meanwhile, despite the rapid progress, there are several outstanding questions regarding the fundamental properties of MBT. A zero magnetic field quantum anomalous Hall effect is difficult to achieve in MBT thin flakes. Magnetic ordering is anticipated to open a band gap on the top surface of MBT; however, the presence or absence of such a magnetic gap is so far controversial.^{3,16–18} Recent studies have revealed that the

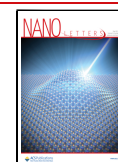
surface of MBT is quite sensitive to air exposure and even to trace oxygen/water levels in a controlled environment such as a glovebox,¹⁹ which could cause complications for the even–odd layer dependent nontrivial phases. It is thus of great practical significance to noninvasively and quickly identify the layer number as well as device degradation to understand the fundamental properties of MBT and the possible application of its versatile topological phases and quantum phase transitions.

In this work, we use Raman scattering to study atomic layers of MBT deposited on gold and SiO_2/Si substrates. A surprisingly strong coupling of MBT flakes to the substrate is observed. This is manifested as an intense breathing mode Raman feature for thin MBT on a substrate that gets significantly suppressed for suspended samples. Our quantitative analysis with a linear chain model shows that the coupling strength between MBT and the substrate is even stronger than the coupling between MBT layers. We further employ Raman scattering to investigate sample degradation under ambient air

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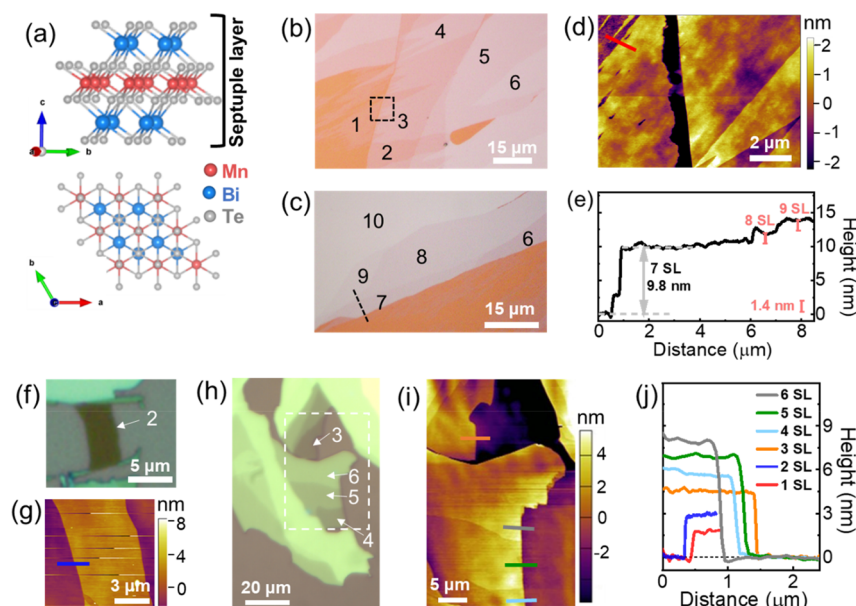


Figure 1. Crystal structure and optical and atomic force microscopy images of MnBi_2Te_4 . (a) Crystalline structure of MnBi_2Te_4 (red, Mn; blue, Bi; gray-white, Te), showing the layered structure of MnBi_2Te_4 along the c axis and the triangular structure in the ab plane. The septuple atomic layers are stacked through vdW forces. The lattice vectors of the unit cell are shown as the arrows denoted by a , b , and c . (b, c) Typical optical images of 1–10 SL MnBi_2Te_4 on a gold substrate. (d) Atomic force microscopy (AFM) micrograph of exfoliated MnBi_2Te_4 flakes with thicknesses of 1–3 SLs. The height profile of 1 SL on the gold substrate along the red line is shown in (e). (e) Height profiles across the line of 7–9 SLs, denoted with corresponding black dashed line in (c). (f, h) Optical images of 2–6 SL MnBi_2Te_4 on a SiO_2/Si substrate. (g, i) AFM micrographs of MnBi_2Te_4 flakes exfoliated on a SiO_2/Si substrate: 2 SL and 3–6 SLs in (g) and (i), respectively. (j) Height profiles across the lines of 1–6 SLs, denoted in red, blue, orange, light blue, green and gray in (d), (g), and (i).

exposure. The low-energy breathing modes are highly sensitive, much more so than the higher energy optical phonons which survive over 50 h of ambient air exposure, indicating that the low-wavenumber Raman for the few-layer MBT provides a practical and useful tool to monitor sample degradation.

The high-quality bulk MBT, with 5% Sb doping, is grown using a conventional high-temperature solution method (see Methods). Atomically thin MBT samples down to 1 SL are fabricated from bulk crystals using a mechanical exfoliation method and deposited onto either gold or SiO_2/Si substrate (details in Methods; additional results on pure MBT, i.e. no Sb doping, are shown in the Supporting Information). Figure 1b,c and Figure 1f,h present typical optical images of MBT flakes on gold and SiO_2/Si substrates, respectively. These thin samples show different optical contrasts for different layer numbers, and their thicknesses are measured by atomic force microscopy (AFM) in a glovebox (see Figure 1d,g,i). The height line profiles of the 1-SL in Figure 1b, 2–6 SL in Figure 1f,h, and 7–9 SL in Figure 1c are shown in Figure 1e,j. From Figure 1e,j, the step height of each additional MBT SL corresponds to a thickness of about 1.4 nm, which is consistent with previous reports.^{20–22} The sample with a height of ~ 1.7 nm from the substrate was assigned to 1 SL; this is slightly larger than 1.4 nm, possibly induced by some adsorbates.

We first characterize the vibrational properties of bulk MBT. Figure 2a shows circular (cocircular, σ^+/σ^+ ; cross-circular, σ^+/σ^-) and linear (parallel, XX; cross, XY) polarization-resolved Raman spectra at room temperature (details are given in Methods). Six intrinsic Raman modes of the bulk samples are observed: three at 46, 109, and 142 cm^{-1} in the σ^+/σ^+ channel, and another three at 27, 68, and 104 cm^{-1} in the σ^+/σ^- channel, indicating good sample crystallinity. In linearly polarized measurements, all six modes are observable in the

XX channel, and the three modes seen in the σ^+/σ^- channel also show up in the XY channel.

At room temperature MBT is paramagnetic. Its unit cell contains only one septuple layer and seven atoms. From a group theory analysis²³ bulk MBT belongs to the point group D_{3d} (space group $R\bar{3}m$), whose character table is shown in Figure 2c. Accordingly, the irreducible representation of MBT atomic displacement for optical phonons at the Γ point is $\Gamma_{\text{opt}} = 3A_{1g} + 3A_{2u} + 3E_u + 3E_g$. Among them, Raman-active modes are $\Gamma_R = 3A_{1g} + 3E_g$. The 2-fold degenerate E symmetry modes represent in-plane vibrations, while the nondegenerate A symmetry mode vibrations are out-of-plane vibrations. On the basis of the circular and linear polarization Raman selection rules, the phonon modes at 46, 109, and 143 cm^{-1} can be assigned as A_{1g} modes and 27, 66, and 104 cm^{-1} as E_g modes. This assignment agrees well with our first-principles calculation results given in Figure 2b, as well as previous studies.^{23–26} We further determine the eigenvectors of Raman modes with first-principles calculations. The atomic displacements of the Raman-active modes are illustrated in Figure 2d,e. The Mn atoms in these modes are stationary, reflecting their even parity nature. These Raman-active vibrations in MBT are somewhat similar to those in materials with similar crystal structures: e.g., Bi_2Te_3 and Bi_2Se_3 .²⁷

Since circular polarization resolved measurements can exclusively distinguish between in-plane and out-of-plane vibrations (Figure 1a),²⁸ in the following we focus on circular polarization-resolved measurements to study MBT thin films. The circular polarization resolved Raman spectra of MBT on a gold substrate are measured from 11 SL to 1 SL as shown in Figure 3a. We clearly observe the same six optical phonon modes $3A_{1g} + 3E_g$ discussed for the bulk, which display no obvious change from 11 SL to 6 SL. Below 5 SL all of them

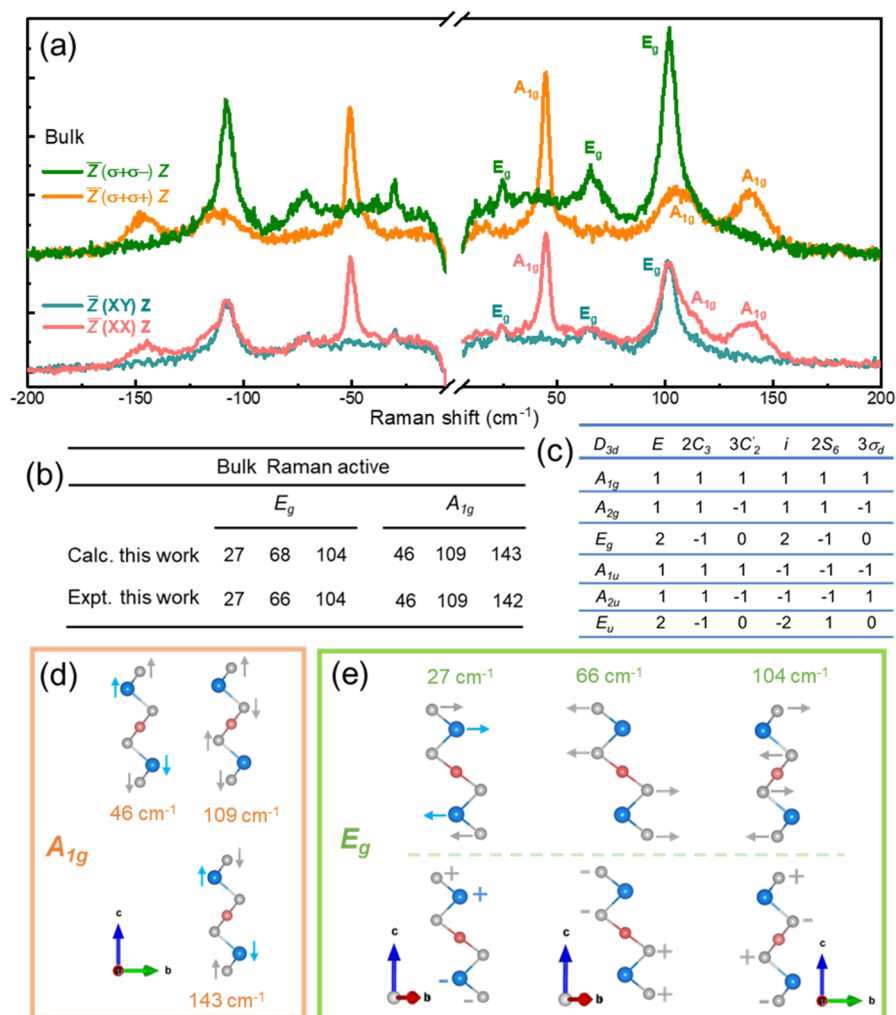


Figure 2. Raman-active vibrational modes of bulk MnBi_2Te_4 . (a) Circularly and linearly polarized Raman spectra of bulk MnBi_2Te_4 at room temperature. (b) Zone-center phonon frequencies (cm^{-1}) of MnBi_2Te_4 . (c) Character table of the D_{3d} point group. (d, e) Displacement schematics of the Raman-active vibrational modes in the bulk sample. The symbols + and – stand for vibrating perpendicularly to the paper, inward and outward, respectively. The long arrows represent the dominant vibrations.

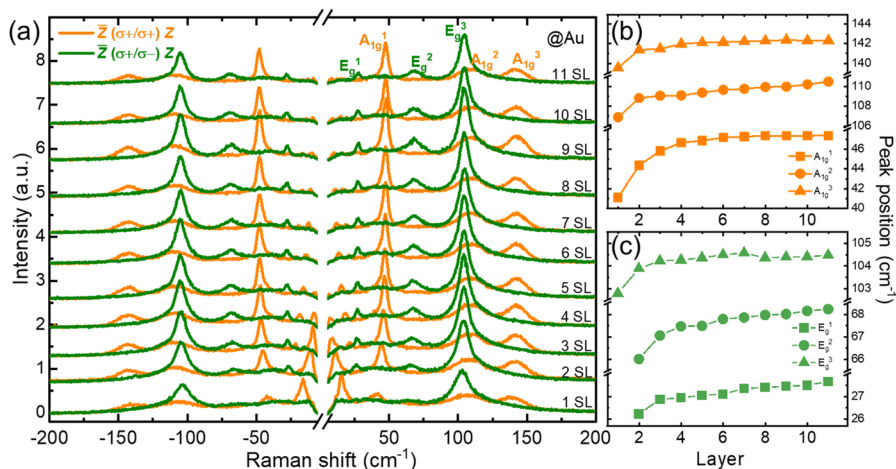


Figure 3. (a) Stokes and anti-Stokes layer dependent Raman spectra of MnBi_2Te_4 on a gold substrate under $\bar{Z}(\sigma^+/\sigma^+)Z$ (orange) and $\bar{Z}(\sigma^+/\sigma^-)Z$ (green) circular polarization configurations in the wavenumber region 6–200 cm^{-1} . (b) A_{1g} mode energy versus thickness. (c) E_g mode energy versus thickness. The layer-dependent Raman spectra for MBT were taken at room temperature.

experience gradual red shift due to a quantum confinement effect. It is noteworthy that the A_{1g}^1 mode at 46 cm^{-1} exhibits

an abrupt intensity decrease from 2 SL to 1 SL and a large red shift of $\sim 6 \text{ cm}^{-1}$ from 11 SL to 1 SL, while the A_{1g}^2 and A_{1g}^3

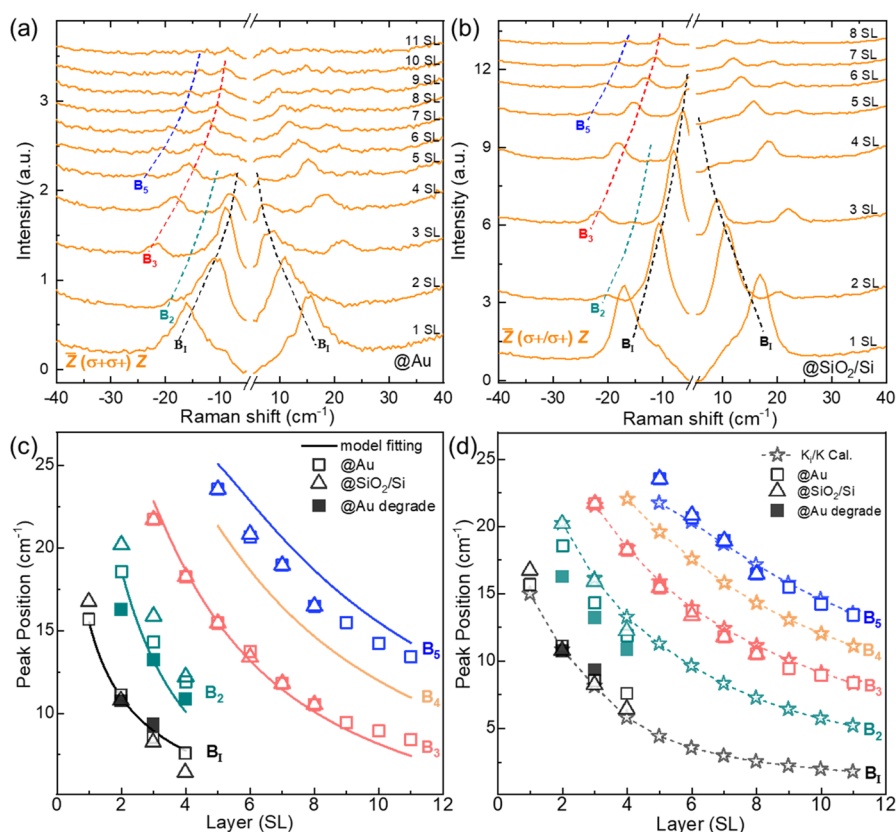


Figure 4. Low-wavenumber Raman spectrum evolution as a function of MnBi_2Te_4 SL layer number at room temperature. (a, b) Low-wavenumber Raman spectra of MnBi_2Te_4 thin films on (a) gold and (b) SiO_2/Si substrates measured using the $\bar{Z}(\sigma^+/\sigma^+)\bar{Z}$ circular polarization configuration. (c) Energy evolutions of measured B_1 , B_2 , B_3 , and B_5 modes in MBT on gold (hollow squares, 1–11 SL) and SiO_2/Si (hollow triangles, 1–8 SL) substrates, as well as the fitting (the solid lines) using the free linear chain model. The solid black and dark green squares are for B_1 and B_2 modes after 2 h degradation, respectively. (d) Comparison between the experimental and the calculated frequencies (star guided by dashed line, 1–11 SL) for the B_1 , B_2 , B_3 , B_4 , and B_5 modes using the linear chain model with $K_{11}/K = 2$ and $K_{12}/K = 0.5$ substrate coupling.

peak red shifts are smaller, $\sim 3 \text{ cm}^{-1}$. The three E_g modes show similar red shifts of $\sim 2 \text{ cm}^{-1}$. These red shifts may come from the increasing electron–phonon coupling due to the quantum confinement effect in thinner layers.^{24,26} We also note that the E_g^1 and E_g^2 modes disappear suddenly for the 1 SL. The reason for this is currently unclear, since from group theory analysis they are expected to be Raman active.

In addition to the six optical phonon modes similar to those in the bulk, additional low-wavenumber Raman modes ($< 30 \text{ cm}^{-1}$) are observed in the thin film samples, attributable to interlayer Raman modes, similarly to other 2D materials.^{29–32} These modes appear mostly in the σ^+/σ^+ channel, suggesting their out-of-plane vibrational nature. Low-energy Raman features (except for the 27 cm^{-1} intralayer optical phonon) in the σ^+/σ^- channel are weak and hard to identify. In the following we focus on the σ^+/σ^+ spectra.

Figure 4a shows the layer-dependent low-wavenumber Raman spectra in the σ^+/σ^+ channel for 1–11 SL MBT on the gold substrate. All of the low-wavenumber Raman modes show significant blue shifts with decreasing layer number and can be classified into four branches we label as B_1 , B_2 , B_3 , and B_5 , guided by the black, green, red, and blue dashed lines, respectively, in Figure 4a. Note that B_2 is not as obvious as the other three branches in Figure 4a but can be more clearly identified for the samples deposited on the SiO_2/Si substrate, as shown in Figure 4b. With an increase in the layer number, the B_2 peak starts to show up from 2 SL, the B_3 peak from 3

SL, and the B_5 peak from 5 SL. These three branches are assigned as interlayer breathing modes. The energies of the breathing modes are very sensitive to the layer number, which makes low-wavenumber Raman spectroscopy a fast and convenient approach for MBT layer number identification. Note that for bulk MBT no low-wavenumber Raman peaks can be observed at all in Figure 2a, which is consistent with the group theory analysis that the interlayer vibrational modes do not exist in bulk MBT, since its unit cell contains only one septuple layer.

Just like the absence of any interlayer Raman modes in the bulk, monolayer MBT is anticipated to have no low-energy breathing or shear modes, as has been demonstrated in other 2D material systems.^{28–34} Interestingly in our data, monolayer MBT on a gold substrate displays a strong Raman feature B_1 at about 16 cm^{-1} , which shows a layer dependence similar to that of other interlayer breathing modes. We have carefully verified this observation on another substrate of SiO_2/Si . As shown in Figure 4b, these B_1 modes are at about the same energy on SiO_2/Si but are more intense and slightly sharper. This makes the B_2 modes more visible than those on a gold substrate. For bilayer MBT deposited on SiO_2/Si , two well-separated breathing modes can be clearly observed. From a general consideration, there should be only one interlayer breathing mode in the bilayer and none in the monolayer. To further investigate the nature of B_1 , we fabricated a four-layer sample that is partially suspended over an etched hole on the silicon

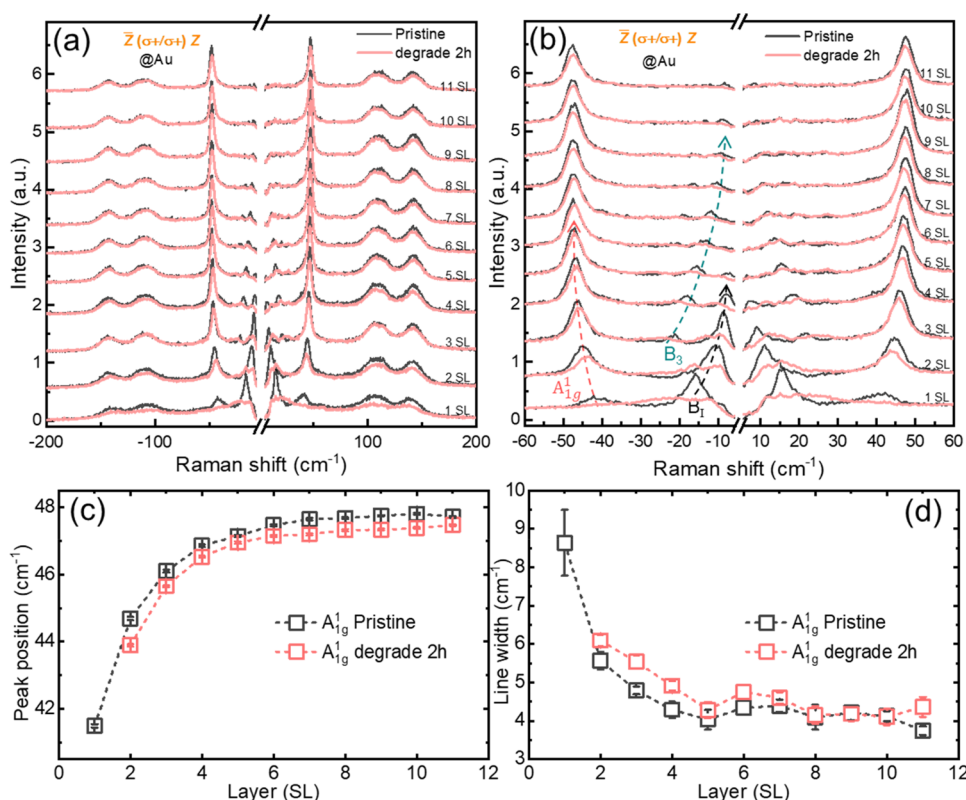


Figure 5. Effect of ambient air exposure on MnBi_2Te_4 thin layers using $\bar{Z}(\sigma^+/\sigma^+)Z$ circular polarization Raman spectroscopy at room temperature. (a) The 1–11 SL Raman spectra comparison of the “pristine” and “2 h degradation” MnBi_2Te_4 samples on a gold substrate. (b) Enlarged low-wavenumber Raman spectra of 1–11 SL MnBi_2Te_4 thin films on a gold substrate. (c, d) Comparison of peak position (c) and line width (d) for the A_{1g} mode in MnBi_2Te_4 (1–11 SL) on a gold substrate before and after degradation.

substrate. When the laser light is centered on the suspended part, the interface mode B_1 is significantly suppressed while other modes are largely the same except for a small red shift, as shown in the table of contents figure. When these results are taken together, the B_1 branch is assigned as the interface breathing mode, which originates from the interaction of few-layer MBT with the substrate.

The energies of the observed breathing modes provide a quantitative measurement of the coupling strength between MBT layers as well as between MBT and the substrate. As the simplest estimation, we can assess the interlayer coupling strength using the bilayer B_2 mode energy $E_{B_2}^{2L}$. From a measured B_2 value of $E_{B_2}^{2L} \approx 19 \text{ cm}^{-1}$, we estimate the MBT interlayer out of plane coupling given by $K = 2\mu(\pi c E_{B_2}^{2L})^2 = 6.4 \times 10^{19} \text{ N/m}^3$, where μ is the mass per unit area of one MBT SL ($\mu = 10.04 \times 10^{-6} \text{ kg/m}^2$), c is the speed of light, and K is the force constant per unit area. A more comprehensive analysis employs the linear chain model²⁹

$$E_{B_\alpha}^{\text{NL}} = \sqrt{\frac{K}{2\mu\pi^2c^2} \left(1 - \cos\left(\frac{(\alpha-1)\pi}{N}\right) \right)} \quad (1)$$

where N denotes the layer number and $\alpha = 1, 2, \dots, N$. The $\alpha = 1$ mode corresponds to the acoustic mode and $\alpha = 2, \dots, N$ correspond to the breathing modes ($K = K_z$) or shear modes ($K = K_x$). This model can fit the measured frequencies of B_2 and B_3 reasonably well with $\alpha = 2, 3$ in Figure 4c, and the resulting force constant K_z is $6.2 \times 10^{19} \text{ N/m}^3$. For B_5 , neither $\alpha = 4$ or $\alpha = 5$ provides an adequate fit, which we will discuss further below. We note that this extracted K_z value is in

reasonable agreement with the DFT calculation of $8.21 \times 10^{19} \text{ N/m}^3$ for Bi_2Te_3 .²⁷ This is not surprising, considering the similarity between MBT and Bi_2Te_3 , especially at the layer interface.

The linear chain model can also be used to extract the MBT-substrate coupling strength

$$E_{B_1}^{\text{NL}} = \sqrt{\frac{K_s}{4N\mu\pi^2c^2}} \quad (2)$$

where N denotes the layer number, μ is the mass per unit area of one MBT SL ($\mu = 10.04 \times 10^{-6} \text{ kg/m}^2$), c is the speed of light, and K_s is the force constant per unit area between MBT and the substrate out-of-plane coupling. We fit B_1 modes in Figure 4c using eq 2, from which we determine K_s to be $8.56 \times 10^{19} \text{ N/m}^3$ for MBT on a gold substrate. This indicates that the coupling between MBT and the substrate is quite strong, with a strength greater than that between MBT layers.

Considering the very large coupling strength between MBT and the substrate, we incorporate in the linear chain model nonzero substrate introduced force constants K_{in} , where n denotes the n th MBT layer from the substrate (details are given in the Supporting Information). Figure 4d illustrates such a fit $K_{11}/K = 2$, $K_{12}/K = 0.5$, and $K = 4.32 \times 10^{19} \text{ N/m}^3$. The fit adequately captures the energy evolution of the three interlayer breathing modes B_2 , B_3 , and B_5 , corresponding to branches of $\alpha = 2, 3, 5$, respectively, in contrast to the fits in Figure 4c. We note that with only K_{11} we can already achieve reasonable fits. Introducing additional K_{in} parameters provide better fits to the multilayer B_1 modes. However, the effect of the additional K_{in} parameters on B_2 , B_3 , and B_5 mode energies

is small. Figure S1a–c in the Supporting Information illustrates fits with one, two, and three substrate coupling parameters, where we have maintained the same $K = 4.32 \times 10^{19}$ N/m³ in all three fits.

The strong coupling with the substrate also greatly disrupts the symmetry of the phonon modes and, in particular, their Raman activity. In the absence of substrate coupling, the $\alpha = 2$, 4 branches of MBT atomic layer breathing modes are Raman active, while $\alpha = 3$, 5 branches are Raman inactive. This contradicts our experimental observations, where $\alpha = 3$ is the most strong MBT breathing mode while the $\alpha = 2$ branch is much weaker, and one can easily miss it for samples deposited on gold. This observation is quite unusual on comparison with other two-dimensional materials such as transition-metal dichalcogenides, where the $\alpha = 2$ breathing mode is the strongest,³³ highlighting the prominent effect of substrate coupling. We note that Raman modes due to coupling with the substrate were also observed in Bi₂Te₃,²⁷ albeit there was a less prominent intensity and no breaking of the breathing mode Raman activity was reported.

We now investigate the effect of ambient air exposure on MBT thin layers using Raman spectroscopy. Figure 5a compares two sets of MBT Raman spectra. “Pristine” corresponds to as-made samples, and “degrade 2 h” corresponds to exposure to ambient air for about 2 h. The degradation has a quite dramatic effect on the monolayer: all of its Raman features are greatly broadened and suppressed, and its A_{1g} mode essentially disappeared. For 2+ layers, despite the degradation, the high-energy optical phonons are remarkably robust. We have performed careful tests for extended air exposure up to 50 h (Figure S2 in the Supporting Information); these optical phonon features remain well-defined. There are noticeable changes in the spectra though. As seen from the enlarged comparison in Figure 5b, the A_{1g} peak experiences a slight red shift and line width broadening after degradation. Detailed quantitative analyses are plotted in Figure 5c,d. From Figure 5b, we also observe that the low-wavenumber breathing modes are much more affected by the degradation. In particular, the B₁ and B₃ modes become less intense. Interestingly, this makes B₂ more visible in 2 SL and 3 SL, providing additional support to our assignment of the B₂ branch in Figure 4. The degradation of MBT is currently of great concern in the research community; our Raman results, particularly the low wavenumber modes, provide a sensitive sensor to monitor device degradation.

We systematically investigated and analyzed the phonon modes in thin films of the magnetic topological insulator MnBi₂Te₄. The layer-number-dependent Raman mode energies provide a direct method to identify the MBT thickness. We discovered an intense ultralow-wavenumber Raman mode in 1–4 SL MBT on gold and SiO₂/Si substrates, which is attributed to substrate–MBT interface coupling. Surprisingly, this coupling is stronger than the interlayer coupling between MBT septuple layers. The implications of such a strong substrate coupling on the MBT magnetic and topological properties have been largely unexplored. In particular, surface electronic states are critical for the band topology of MBT thin films and so far theoretical calculations have typically neglected the effect of the substrate. Experimentally conflicting results and interpretations exist regarding the zero quantum anomalous Hall plateau in even and odd layers of MBT, for which the effect of the substrate has not been carefully considered. Finally, we observed the degradation in thin layers

by the change in low-wavenumber Raman modes, suggesting the instability of MBT thin layers in the air. Thus, the layer-dependent Raman study of MBT provides a facile tool to confirm the layer number and monitor sample degradation, which is useful for future quantum phenomena studies.

METHODS

Sample Preparation. High-quality single crystals of MBT with 5% Sb doping were grown by a conventional high-temperature solution method.^{35–37} The Mn (purity 99.98%), Bi (99.999%), Sb (99.99%) and Te (99.999%) blocks were weighed and ground in an agate mortar and then placed in an alumina crucible. The alumina crucible was sealed in a quartz tube in an argon environment. The assembly was first heated in a box furnace to 950 °C, held for 10 h, then subsequently cooled to 700 °C over 10 h and further cooled slowly to 575 °C in 100 h. After this heating procedure, the quartz tube was taken out quickly and the contents were then decanted into a centrifuge to remove the excess flux from the single crystals. The thin samples were fabricated by mechanically exfoliating the flakes in a glovebox directly on two different substrates: Au (5 nm)/Cr (3 nm)/SiO₂/Si (gold) and SiO₂/Si. For the MnBi₂Te₄ flakes on SiO₂/Si, poly(methyl methacrylate) (PMMA) was spin-coated on the sample inside the glovebox right after exfoliation. After optical measurements, the PMMA was washed away for AFM measurements. All the exfoliation, spin-coating/washing with PMMA, and AFM measurement processes were done inside a glovebox, and these samples were not exposed to air. The MnBi₂Te₄ flakes on a gold substrate were not protected by PMMA, and there is a brief exposure to the air when the sample is transferred from the glovebox to a cryostat for optical measurements. Crystals without Sb doping were grown and exfoliated similarly. See Figure S3 in the Supporting Information for a comparison of Raman spectra of the two types of samples. The suspended 4 SL MnBi₂Te₄ sample shown in the table of contents graphic was made using crystals without Sb doping.

Raman Spectroscopy. The circular polarization resolved Raman measurements were performed with a micro-Raman spectrometer (Horiba iHR550) equipped with a liquid-nitrogen-cooled CCD detector. The excitation laser (632.8 nm) was first guided through a vertical linear polarizer followed by a quarter-wave plate to achieve σ^+ circular polarization. The circular polarization of the excitation light was confirmed at the sample position. All Raman measurements were conducted in the backscattering configuration. The backscattered Raman signal going through the same quarter-wave plate was collected and analyzed with a half-wave plate and a linear polarizer. Rotation of the half-wave plate at different angles enabled us to obtain detailed information on the helicity of the scattered light. The scattered light passed through two ultranarrow band notch filters to suppress the Rayleigh scattering light, which enables low-wavenumber measurements down to 5 cm^{−1}. The laser power was kept below 0.5 mW. The layer-dependent Raman spectra for MBT were obtained at room temperature. For optical measurements, we took the sample out of the glovebox, quickly put it into the vacuum chamber, and kept it in the vacuum chamber at 10^{−6} Torr. When the degradation effects were studied, the sample was exposed to the air before each measurement. In the text, “ambient air” refers to room-temperature, unfiltered air. The humidity in the laboratory was around 60%.

DFT Calculations. First-principles calculations were performed within the density functional theory framework using the projected augmented-wave (PAW) method³⁸ as implemented in the Vienna *ab initio* simulation package (VASP).^{39,40} The exchange-correlation term was treated in the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE).⁴¹ The Kohn–Sham orbitals were expanded in a plane wave basis set with an energy cutoff of 450 eV. All of the structures were optimized until the Hellman–Feynman forces on each atom were smaller than 0.001 eV/Å (10^{-5} eV/Å for phonon calculations), and the energy convergence was considered reached when the energy difference was below 10^{-7} eV between two consecutive self-consistent steps. Spin-polarized GGA+U calculations were performed with a U_{eff} value of 5 eV for Mn atoms, since DFT often provides an unsatisfactory description for such a strongly correlated transition-metal system with localized *d* orbitals. A $15 \times 15 \times 15$ Γ -centered *k*-point mesh was used for the *k*-point sampling and Brillouin zone integration. Partial occupancies were handled using Gaussian smearing with a broadening width of 0.05 eV. van der Waals corrections were considered using the DFT-D3 method.⁴² The phonon modes and frequencies were determined by the frozen phonon method as implemented in the PHONOPY⁴³ code at the Γ point.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.1c04194>.

Detailed description of the linear chain model fitting, Raman spectra of samples degraded up to 50 h, Raman spectra of samples without Sb doping, and RMCD of MnBi₂Te₄ atomic layers (PDF)

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Notes

The authors declare no competing financial interest.

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