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Structural and electronic properties of manganese-doped Bi$_2$Te$_3$ epitaxial layers

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Abstract

We show that in manganese-doped topological insulator bismuth telluride layers, Mn atoms are incorporated predominantly as interstitials in the van der Waals gaps between the quintuple layers and not substitutionally on Bi sites within the quintuple layers. The structural properties of epitaxial layers with Mn concentration of up to 13% are studied by high-resolution x-ray diffraction, evidencing a shrinking of both the in-plane and out-of-plane lattice parameters with increasing Mn content. Ferromagnetism sets in for Mn contents around 3% and the Curie temperatures rises up to 15 K for a Mn concentration of 9%. The easy magnetization axis is along the $c$-axis perpendicular to the (0001) epitaxial plane. Angle-resolved photoemission spectroscopy reveals that the Fermi level is situated in the conduction band and no evidence for a gap opening at the topological surface state with the Dirac cone dispersion is found within the experimental resolution at temperatures close to the Curie temperature. From the detailed analysis of the extended $x$-ray absorption fine-structure experiments (EXAFS) performed at the MnK-edge, we demonstrate that the Mn atoms occupy interstitial positions within the van der Waals gap and are surrounded octahedrally by Te atoms of the adjacent quintuple layers.

1. Introduction

Bismuth telluride (Bi$_2$Te$_3$) is a prototypical example for a three-dimensional (3D) topological insulator with a gapped bulk band structure and a topological two-dimensional (2D) surface state with Dirac-like energy–momentum dispersion and spin–momentum locking [1–3]. The surface states are protected by time-reversal symmetry and are immune to surface impurities and backscattering. When 3D transition metals such as Mn, Fe, Cr or V are incorporated as magnetic dopants [4], however, their local exchange fields can break time reversal symmetry and thus may lift the degeneracy of the Dirac points with a concomitant gap opening of the topological surface state [1–3, 5–8]. In addition, novel phenomena arising from the interaction between topologically protected states and ferromagnetic order have been theoretically predicted [1–3], including the topological magneto-electric effect, the quantum anomalous Hall effect, half-integer charges at magnetic domain boundaries [3]; some of these were already observed experimentally [9].

The solubility of magnetic ions in topological insulators is typically limited to a few percent and Mn-doped Bi$_2$Te$_3$ crystals and thin films with concentrations of up to 10% were found to be ferromagnetic with Curie temperatures around 10 K [10–16]. In some of these works, Mn-doped Bi$_2$Te$_3$ showed $p$-type conduction [10, 11] or at least a weak acceptor-like behavior of Mn [17] as evidenced by a downward shift of the Fermi level [10, 11, 17]. From this it was concluded that Mn ions preferentially occupy substitutional Bi lattice sites, forming...
(Bi$_{1-x}$Mn$_x$)$_2$Te$_3$ [11]. However, the downward shift of the Fermi level observed by angle-resolved photoelectron spectroscopy (ARPES) was rather small, i.e., much less than expected for purely substitutional Mn incorporation. In most other works, Mn-doped Bi$_2$Te$_3$ even retained its n-type character [14, 17], indicating a non-substitutional Mn incorporation. Indeed, recent compositional analysis of bulk crystals has revealed that Mn may also be incorporated interstitially as in Mn$_x$Bi$_{2-x}$Te$_3$ [14], but no precise information on the actual incorporation sites was reported. It has also been suggested that Mn may incorporate in excess Bi–Te double layers [12, 15] easily formed in bismuth telluride when grown under tellurium deficient conditions [12, 18, 19]. Thus, the mechanism of Mn incorporation has been rather unclear. Nevertheless, in all cases, Mn doping has resulted in ferromagnetic behavior, but without any remarkable dependence of the Curie temperatures on the carrier concentration [11, 14, 15, 20].

Due to the complex crystal structure of Bi$_2$Te$_3$ with its large hexagonal unit cell consisting of three Te–Bi–Te quintuple layers (QLs) bonded together across a van der Waals (vdW) gap, several different possible lattice sites exist for the incorporation of magnetic dopants. These include substitutional incorporation for Bi atoms within the QLs as well as interstitial incorporation within the quintuple layers or within the van der Waals gap between the QLs in different local coordinations. Evidently, different lattice sites for Mn incorporation are expected to result in quite different electronic and magnetic properties of the material [16] and, thus, to a different influence on the topological surface states. Therefore, the determination of the actual position of Mn in the lattice of Bi$_2$Te$_3$ is of utmost importance for further studies on its striking topological properties and their interplay with ferromagnetism.

To resolve this issue, in this paper we report a detailed study on the lattice sites of Mn incorporation in Bi$_2$Te$_3$. For this purpose, we performed a systematic investigation on a series of Mn-doped epitaxial Bi$_2$Te$_3$ layers using high-resolution x-ray diffraction (XRD) and extended x-ray absorption fine-structure (EXAFS) measurements. These were complemented by magnetic characterization using a superconducting quantum interference magnetometer (SQUID), which revealed that the layers are ferromagnetic with Curie temperatures of up to 15 K. Angle-resolved photoelectron spectroscopy (ARPES) shows no opening of a gap of the topological surface state at temperatures down to 12 K. By detailed theoretical analysis of the XRD and EXAFS spectra, we show that Mn is incorporated predominantly as interstitial in octahedral positions within the vdW gaps of Bi$_2$Te$_3$, i.e., between two Te layers of adjacent QLs.

2. Growth

Mn-doped Bi$_2$Te$_3$ layers were grown by MBE on (111)-orientated BaF$_2$ substrates using a compound bismuth telluride effusion cell, a Mn cell, and an additional tellurium cell for stoichiometry control. The in-plane lattice-constant of BaF$_2$ (111) is almost exactly lattice-matched to the lattice constant $a$ of the hexagonal basal planes of Bi$_2$Te$_3$ (lattice-mismatch less than 0.04 %) and, thus, growth proceeds with the $c$-axis orientation perpendicular to the surface [18]. A whole series of samples was grown where the Mn concentration was varied between 0 and 13%. For all samples, the substrate temperature was 330 °C and a background pressure of ≤ 5 × 10$^{-10}$ mbar was maintained during growth. The flux rates from the sources were measured using a cooled quartz crystal microbalance moved into the substrate deposition. The mass deposition rates were converted into the flux rate of atoms arriving at the surface using the density and molar mass of each component. The total growth rate of (Bi,Mn)$_2$Te$_3$ was ~0.15 QL$^{-1}$ or ~1.5 Å s$^{-1}$ and a high excess tellurium flux above 2.5 Å/s was provided during growth, corresponding to an overall Te-to-Bi(Mn) flux ratio of ~5:1. Under these conditions, stoichiometric Bi$_2$Te$_3$ epitaxial layers are obtained with no indication of formation of Bi–Te double layers, as shown in detail by our previous work [18, 19]. The Mn concentration in the samples varied from $x_{\text{Mn}}$ = 0 to 13% and was determined by the measured Mn-to-Bi flux ratios, where we defined $x_{\text{Mn}}$ as the ratio of Mn atoms relative to the number of the sum of Bi and Mn atoms. Thus, the overall layer composition can be represented by Mn$_x$Bi$_{2-x}$Te$_3$, where $x$ ≤ 1.5 depends on the type of Mn incorporation. For purely substitutional Mn, $x$ = 1.5, whereas for purely interstitial Mn, $x$ = 1.5(1 − $y$), provided that the 2:3 ratio between Bi and Te is retained. Nice streaked reflection high-energy electron diffraction (RHEED) patterns were observed during growth for all samples irrespective of the Mn content, indicating 2D growth in all cases. All layers exhibit n-type conduction with an electron density of ~10$^{19}$ cm$^{-3}$ that does not change significantly with Mn content.

3. Structural characterization by x-ray diffraction

The rhombohedral crystal structure of Bi$_2$Te$_3$ with R $ar{3}$ m symmetry and the different possible incorporation sites of Mn are illustrated in figure 1. The unit cell with the hexagonal lattice parameters $a$ = 0.4385 nm and $c$ = 3.051 nm [18] consists of fifteen (0001) hexagonal lattice planes grouped in three Te(1)–Bi–Te(2)–Bi–Te(3) QLs stacked in ABCABC… sequence [see figure 1(a)]. The QLs are weakly bonded together by a double layer of

$y$
Te atoms forming the vdW gaps of the structure. Because of the large inter-planar distance of the vdW gap, interstitial positions within the vdW gaps are expected to be favorable for Mn incorporation. Two possible interstitial positions in the vdW gaps exist, either tetrahedral or octahedral sites with 4, respectively, 6 nearest neighboring Te atoms, as illustrated in figures 1(b) and (c), respectively. Substitutional Mn is expected to reside on Bi atom positions within the QLs. The corresponding expected nominal nearest neighbor (NN) distances for these three different incorporation sites are listed in table 1, together with the NN distances of Mn in Bi–Bi DL in Bi₂Te₃−δ, as proposed by [12, 15]. Also listed are the NN Mn–Te distances in various other manganese telluride compounds (zinc blende (zb), wurzite (wz) and hexagonal MnTe (NiAs type) as well as cubic MnTe₂ (pyrite type)) are listed.

| Mn position                                      | NN distance (nm) |
|-------------------------------------------------|------------------|
| Substitutional Mn on Bi site in Bi₂Te₃          | 0.3032           |
| Tetrahedral Mn as interstitial in vdW gap       | 0.2542           |
| Octahedral Mn as interstitial in vdW gap        | 0.2885           |
| Substitutional Mn in Bi–Bi DL in Bi₂Te₃−δ       | 0.3268           |
| Tetrahedral Mn in zb MnTe                       | 0.2774           |
| Tetrahedral Mn in wz MnTe                       | 0.2513           |
| Octahedral Mn in hexagonal MnTe (NiAs type)     | 0.2924           |
| Octahedral Mn in MnTe₂ (pyrite type)            | 0.2904           |

In order to study the crystal structure of Mn-doped Bi₂Te₃, high resolution x-ray diffraction experiments were performed using CuKα radiation and a diffractometer equipped with multilayer parabolic optics, a 4 × (220) Ge Bartels monochromator and a 2 × (220) Ge analyzer crystal. Symmetrical (000 L) scans of the

Figure 1. (a) Hexagonal unit cell of Bi₂Te₃ consisting of three Te(1)–Bi–Te(2)–Bi–Te(1) quintuple layers (QL) stacked in an ABCABC… sequence. The dotted lines denote the vdW gaps between two adjacent Te layers. Tetrahedral and octahedral interstitial positions in a vdW gap are illustrated in panels (b) and (c), respectively. (d) Unit cell of the cubic pyrite MnTe₂, phase [23, 24], in which the Mn atoms are also octahedrally coordinated. In (e) the atom positions around an octahedral coordinated Mn in the vdW gap in Bi₂Te₃ is compared to the Te positions in the first coordination shell of MnTe₂. The green lines denote the connections of the central Mn atom to the Te atoms in the first coordination shell.
samples with different Mn content are presented in figure 2(a), where the scattered intensities are plotted as functions of the length \( Q \) of the scattering vector. The pure Bi\(_2\)Te\(_3\) layer exclusively shows the diffraction maxima with \( L = 9, 15, 18, 21, \ldots \) characteristic for the perfect Bi\(_2\)Te\(_3\) phase (see [18, 19] for details), evidencing the absence of additional Bi–Bi double layers in the structure [19]. With increasing Mn content \( x_{\text{Mn}} \), the diffraction maxima are shifted, and additional satellite maxima appear as indicated by the blue arrows in figure 2.

To analyze the diffraction data, we start with the diffraction data of the non-doped Bi\(_2\)Te\(_3\) sample \( (x_{\text{Mn}} = 0) \). The unit cell of Bi\(_2\)Te\(_3\) is non-primitive and consists of three identical QLs mutually shifted in a lateral direction [see figure 1(a)]. Therefore, in symmetric \( L(000) \) diffraction [figure 2(a)], the structure factors of the quintuplets are identical and the effective structure unit of the crystal is one-third of the hexagonal unit cell \( c \) with a height \( d_{\text{QL}} = c/3 \). Thus, only diffraction maxima \( L = 3, 6, 9, \ldots \) are allowed and the positions of these maxima are indicated by red dotted lines in figure 2. Ignoring the small differences in the inter-planar distances within the QLs and between them [19], Bi\(_2\)Te\(_3\) can be considered as a periodic sequence of 2D hexagonal basal planes of atoms with ABC... stacking similar to a face-centered cubic lattice. In this layer sequence, the (Bi,Te) occupation of the lattice positions varies periodically along the [0001] growth direction. Replacing the true atoms in the lattice by a virtual ‘mixture’ of Bi and Te, the diffraction maxima of such a crystal will appear at \( Q = 2\pi n/d \), where \( n \) is an integer and \( d \) is the mean distance of the (0001)-planes of the virtual crystal, i.e., the average distance between the basal planes in the actual lattice. Since \( d = d_{\text{QL}}/5 = c/15 \), the diffraction maxima of this virtual lattice appears at \( L = 15, 30, 45, \ldots \) (red arrows in figure 2). As a result, these are the major diffraction maxima, whereas all other (000) maxima with \( L = \ldots, 9, 12, 18, 21, 24, 27, 33, \ldots \) can be considered as modulation maxima caused by the periodic modulation of the occupation of the lattice planes either by Te or Bi atoms. Taking into account the modulation of the periodic sequence of QLs, we thus obtain the diffraction pattern of the Bi\(_2\)Te\(_3\) phase, and the corresponding additional peaks are denoted by green arrows in figure 2. From this analysis, it follows that only the maxima \( L = 15, 30 \) (red arrows) can be used for determination of the average spacing \( d \) of the lattice planes, i.e., for derivation of the average lattice constant along the \( c \)-direction.

As shown in figure 2, with increasing Mn concentration, additional (satellite) maxima appear in the diffraction spectra (blue arrows). These satellites are caused by an additional modulation of the structure along the growth direction with a period \( L_{\text{mod}} = 2\pi/\Delta Q \) that is given by the distance \( \Delta Q \) between these satellite maxima. This is similar to the case of the tellurium deficit in the Bi\(_2\)Te\(_{3-\delta}\) structures, where additional Bi–Bi double layers are randomly inserted between the quintuple layers [19]. In Mn-doped Bi\(_2\)Te\(_3\), we assume that this

![Figure 2](image-url)
modulation comes from Mn incorporated in the vdW gaps between the QL layers, which changes the distance between the facing Te–Te layers in the gap in a modulated manner. To support this idea, a series of diffraction curves was simulated assuming that after every \( m \)th quintuple layer the distance of the Te–Te vdW gap and the distance between the first Te layer and the subsequent Bi layer is changed by \( \Delta d_{\text{Te-Te}} \) and \( \Delta d_{\text{Te-Bi}} \), respectively. We averaged the diffracted intensity over random values of \( m \) with an average value of \( \langle m \rangle \) and a root-mean square (rms) deviation \( \sigma_m \) with respect to this value. The such-created modulation period is related to \( m \) by \( L_{\text{mod}} = 2d_{\text{QL}}/\langle m \rangle \). The corresponding simulation results for different \( \Delta d \) and \( \sigma_m = 0.8 \) are presented in figure 2(b), where \( \Delta \langle d \rangle \) denotes the deviation of the mean inter-planar distance from the value in the pure Bi\(_2\)Te\(_3\) phase. From the structure of Bi\(_2\)Te\(_3\), it follows that \( \Delta \langle d \rangle = (\Delta d_{\text{Te-Te}} + 2\Delta d_{\text{Te-Bi}})/\langle 5 \rangle \). The simulations reveal that the diffraction curves sensitively depend on \( \Delta \langle d \rangle \); the dependence on the individual deviations \( \Delta d_{\text{Te-Te}}, \Delta d_{\text{Te-Bi}} \) turned out to be negligible for \( |\Delta d_{\text{Te-Te}}, \Delta d_{\text{Te-Bi}}| \lesssim 0.005 \text{ nm} \).

As illustrated by figure 2(b), with this model, key features of the diffraction curves can be explained, such as the appearance of the additional modulation peaks (blue arrows in figure 2) with increasing Mn concentration, as well as the shifts of the diffraction peaks. Still, the model is too simple to exactly reproduce the shapes of the diffraction curves. From the simulations, it follows that with increasing negative values of \( \Delta \langle d \rangle \), the lattice constants \( c \) decreases, and, consequently, the ‘true’ diffraction peaks (red and green arrows) move to larger \( Q \).

With increasing \( \Delta \langle d \rangle \), the envelope curve of the diffraction maxima changes due to the change of the form factor \( d \), the mean modulation period \( \sigma_m = 0.8 \) from the average value determined from the positions and widths of the satellite peaks in figure 2.

For further evaluation of the experimental data, for each sample we have determined the mean inter-planar distances \( \langle d \rangle \), the mean modulation period \( \langle m \rangle \), as well as its rms deviation \( \sigma_m \) from the positions of the ‘true’, respectively, additional satellite peaks. In addition, the in-plane lattice parameter \( a \) of the layers was determined from the peak positions of the asymmetric (1014) diffraction peaks measured by reciprocal space mapping [18]. The results are listed in table 2 and plotted in figure 3 as a function of the Mn concentration \( x_{\text{Mn}} \). Clearly, the vertical average inter-planar distance \( \langle d \rangle \) and thus, the lattice parameter \( c \), as well as the in-plane lattice parameter \( a \) continuously decrease with increasing Mn content. This indicates that Mn is indeed incorporated in the bismuth telluride host lattice, and that Mn does not induce the formation of additional Bi–Bi double layers between the quintuplets as proposed by Lee et al [15]. As in the latter case, the in-plane lattice constant \( a \) should

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
x_{\text{Mn}} \text{%} & a \text{ (nm)} & \langle d \rangle \text{ (nm)} & \langle m \rangle & \sigma_m \text{/}\langle m \rangle & T_C \text{ (K)} \\
\hline
0 & 0.4380 ± 0.0001 & 3.0508 ± 0.0015 & — & — & 0 \\
1 & 0.4380 ± 0.0003 & 3.0399 ± 0.0045 & 13.8 ± 1.0 & 0.16 ± 0.02 & 0 \\
3 & 0.4374 ± 0.0003 & 3.0101 ± 0.0075 & 2.6 ± 1.0 & 0.18 ± 0.02 & 7.5 \\
6 & 0.4368 ± 0.0006 & 3.0098 ± 0.0105 & 2.2 ± 1.0 & 0.16 ± 0.02 & 10 \\
9 & 0.4365 ± 0.0006 & 2.9850 ± 0.0150 & 2.0 ± 1.0 & 0.16 ± 0.02 & 15 \\
13 & 0.4340 ± 0.0010 & — & 1.4 ± 2.0 & 0.25 ± 0.04 & 12 \\
\hline
\end{array}
\]

Figure 3. (a) Mean inter-planar distance \( \langle d \rangle \) (blue) and the in-plane lattice parameter \( a \) of Mn-doped bismuth telluride plotted as a function of Mn concentration obtained by x-ray diffraction. The horizontal dotted lines represent the nominal values of pure Bi\(_2\)Te\(_3\). (b) Mean modulation periods \( \langle m \rangle \) (blue) and their rms deviation \( \sigma_m \) from the average value determined from the positions and widths of the satellite peaks in figure 2.
increase [19] rather than decrease with increasing alloy concentration. No additional modulation periodicity is found for \( x_{\text{Mn}} = 0 \). For \( x_{\text{Mn}} = 1\% \), the modulation period \( (m) \) is about 14, i.e., very large, but it rapidly decreases for higher \( x_{\text{Mn}} \) to \( (m) \approx 2.5 \) without significant further changes. For \( x_{\text{Mn}} = 13\% \), the value of \( (d) \) cannot be determined, since its diffraction curve does not exhibit the ‘true’ red- and green-arrow peaks and the diffraction maxima become very broad, so that the uncertainty in determining \( (m) \) is rather large. As in this case, the Mn concentration is close or even above the solubility limit, so it is likely that for this structure already some phase separation has occurred, with the formation of small amounts of secondary Mn–Te phases, leading to a structural degradation. However, the amount of secondary phases must still be small, as no extra diffraction peaks for secondary phases are observed in the diffraction data.

4. Magnetic and electronic properties

The magnetic properties of the Mn-doped Bi\(_2\)Te\(_3\) epilayers were characterized by SQUID magnetization measurements, where the magnetization \( M(H) \) and \( M(T) \) were recorded as a function of temperature from 2 K to 300 K, and magnetic field \( H \) applied either perpendicular (out-of-plane) or parallel (in-plane) to the surface of the films. The diamagnetic contribution of the BaF\(_2\) (111) substrate was derived from \( M(H) \) curves at 300 K and was subtracted from all data. Note, that identical sample pieces were used for in-plane and out-of-plane measurements, as described in [25]. Figure 4 shows the in-plane and out-of-plane magnetization curves for the 4% and 9% Mn-doped Bi\(_2\)Te\(_3\) samples at 2 K, representative for the entire sample series. For both samples, a clear hysteresis is observed, evidencing ferromagnetic properties, and in both cases, the c axis, i.e., the out-of-plane orientation, is clearly the easy axis of magnetization, similar to the findings of bulk samples [11, 14] and films grown on InP (111) [15]. The inset of figure 4(a) shows the dependence of the Curie temperature \( T_C \) on \( x_{\text{Mn}} \) estimated from the \( M(T) \) measurements. \( T_C \) increases from 8.5 K for \( x_{\text{Mn}} = 3\% \) up to 15 K for \( x_{\text{Mn}} = 10\% \), consistent with previous findings [14, 15]. At high \( x_{\text{Mn}} \), a slight decrease in \( T_C \) is observed, accompanied by a finite positive slope in the 2 K \( M(H) \) curves at a high magnetic field above 1 T (not shown). We tentatively ascribe this observation to the onset of the formation of a secondary antiferromagnetic Mn-containing phase such as hexagonal MnTe or cubic MnTe\(_2\), which reduces the effective concentration of ferromagnetic Mn incorporated in the bismuth telluride host. A detailed analysis of this secondary phase will be reported elsewhere.

To characterize the topological surface state and electronic band structure of the epitaxial layers, ARPES investigations were performed at the beamline BL-1 of the Hiroshima Synchrotron Radiation Center (HiSOR) at Hiroshima University, with a set-up described in detail elsewhere [26]. In order to avoid surface deterioration during air exposure of the samples during transportation, the samples were capped in situ in the MBE chamber by a Te/Se double layer after cooling to room temperature. This provides effective protection against surface oxidation. Prior to ARPES measurements, the samples were decapped in UHV by annealing at 130 °C and 250 °C for 15 minutes to completely desorb the Se and Te capping layers and regain a clean epilayer surface. This was checked and confirmed by low-energy electron diffraction. Low-temperature ARPES data recorded at 12 K for the series of samples with various \( x_{\text{Mn}} \) from 0 up to 13% are shown in figure 5.

For all Mn-doped bismuth telluride layers, the ARPES data shows a well-pronounced Dirac cone of their topological surface states up to highest \( x_{\text{Mn}} \) of 13%, i.e., no apparent gap opening at the Dirac point is observed within the experimental resolution of 30 meV. This is in contrast to previous results for Bi\(_2\)\(_{1-x}\)Mn\(_x\)Se\(_3\) reported

![Figure 4](image-url)
by Xu et al. [27], who have found a gap opening even above the bulk ferromagnetic Curie temperature, which was attributed to an enhanced ferromagnetic order at the surfaces. This is not found for our Mn-doped Bi\(_2\)Se\(_3\) epilayers at \(T = 12\) K. However, since the theoretically predicted gap opening is below 20 meV in the ferromagnetic phase for substitutional Mn incorporation [8], our observations do not completely rule out such an effect. It is noted that the absence of a gap opening as revealed by our experiments is in agreement with observations for bulk Bi\(_{1-x}\)Mn\(_x\)Te\(_3\) [10, 11] and moreover, it has been theoretically predicted that under certain conditions, the topological surface states may survive upon moderate Mn doping [8]. For all our samples, the Fermi energy is within the conduction band (dashed horizontal lines in figure 5) irrespective of the Mn concentration. Thus, we do not observe a notable p-doping of bismuth telluride by Mn incorporation, i.e., Mn does not show an acceptor-like behavior. This is a first indication that Mn is not substitutionally incorporated on Bi lattice sites.

5. X-ray absorption spectroscopy

To gain further insights on the Mn incorporation, we have performed EXAFS experiments at the BM32 beamline of the European Synchrotron Radiation Facility in Grenoble. EXAFS measurements were performed at the MnK-edge (6.55 keV) at the incidence angle of 2.5° with respect to the sample surface. The MnK\(\alpha\) fluorescence signal was detected using an energy dispersive detector placed nearly horizontally to the sample in order to suppress the elastic scattering signal of the horizontally polarized synchrotron x-ray beam. Several spectra were averaged, and the normalized EXAFS part \(\chi(E)\) was extracted using the Athena software [28] as \(\chi(E) = (\mu(E) - \mu_0(E))/\Delta \mu_0\), where \(\mu(E)\) denotes the measured absorption spectrum, \(\mu_0(E)\) is its smooth background corresponding to absorption of an isolated (‘bare’) Mn atom and \(\Delta \mu_0\) is the height of the absorption edge. The photon energy is transformed into wave vector \(k\) of the excited electron as \(E = E_{edge} + h^2k^2/(2m_e)\), where \(E_{edge}\) is the energy of the absorption edge and \(m_e\) is the electron mass. Normalized EXAFS spectra for the samples with different Mn concentration are presented in figure 6. Evidently, the spectra collected from various samples do not show significant differences, indicating that the Mn incorporation does not depend much on the Mn content of our samples. The signal from the sample with Mn content of \(x_{Mn} = 1\) % was too low compared to the background noise, so we did not include this sample in the data evaluation.

For the determination of the preferentially occupied Mn lattice sites, extensive \textit{ab initio} simulations of the EXAFS spectra using the FEFF9 software [29] were carried out. In the simulations, octahedral and tetrahedral interstitial Mn positions within the vdW gaps, as well as substitutional Mn on Bi lattice sites, as well as

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Figure 5. ARPES spectra at 12 K for Mn-doped Bi\(_2\)Te\(_3\) layers with \(x_{Mn} = 0\) % (a), 4% (b), 6% (c), 9% (d), and 13% (e). The data was measured along the K-\(\Gamma\)-K cut of momentum space at \(h\nu = 50\) eV. (f) Energy distribution curves (EDC) of the sample with \(x_{Mn} = 13\) % with an obvious maximum in the Dirac point. The horizontal dotted lines denote the Fermi energy.
substitutional Mn in extra Bi double layers between QL layers as suggested by [12, 15] were considered. For further comparison, simulations were also performed for various manganese telluride phases, including zb, wz and hexagonal MnTe (NiAs-type) lattices, as well as cubic pyrite MnTe2 (see figure 1) with the NN-distances listed in table 1. For all possible Mn sites, series of simulations were performed using variable cluster sizes up to 1.2 nm. The simulations showed that increasing the cluster radius beyond 0.9 nm did not cause any changes of the calculated results. Therefore, a cluster size of 0.9 nm was used for all simulations, which included 85 to 140 atoms, depending on the lattice structure assumed. This cluster size is typical for these types of simulations.

In figure 7, the experimental EXAFS spectrum for the sample with $x_{\text{Mn}} = 9\%$ is compared with spectra derived from \textit{ab initio} atomistic simulations (red lines) assuming different Mn positions in the Bi$_2$Te$_3$ lattice from Mn in the vdW gap to substitutional Mn in the QLs, or Bi–Bi DLs as suggested by [12, 15]. Also plotted for comparison, are the simulated spectra (blue lines) for various MnTe (zb, wz, hexagonal) and MnTe$_2$ (pyrite) lattices described in the text. The spectra are shifted vertically for clarity.

substitutional Mn in extra Bi–Bi double layers between QL layers as suggested by [12, 15] were considered. For further comparison, simulations were also performed for various other manganese telluride phases, including zb, wz and hexagonal MnTe (NiAs-type) lattices, as well as cubic pyrite MnTe$_2$ (see figure 1) with the NN-distances listed in table 1. For all possible Mn sites, series of simulations were performed using variable cluster sizes up to 1.2 nm. The simulations showed that increasing the cluster radius beyond 0.9 nm did not cause any changes of the calculated results. Therefore, a cluster size of 0.9 nm was used for all simulations, which included 85 to 140 atoms, depending on the lattice structure assumed. This cluster size is typical for these types of simulations.

In figure 7, the experimental EXAFS spectrum for the sample with $x_{\text{Mn}} = 9\%$ is compared with the results of the FEFF9 simulations for the different Mn incorporation sites. It turns out that only for the octahedral interstitial Mn positions within the vdW gap (top curve in figure 7) the measured data is reproduced very well by the simulation, while for Mn incorporation at the other positions, the simulations strongly differ from the experimental spectra. The same result was also found for all other samples with different Mn concentrations. Thus, we conclude that Mn in Bi$_2$Te$_3$ is predominantly incorporated in the middle of the van der Waals gap between the QLs in octahedral coordination—at least under the given growth conditions. In the further data evaluation we therefore consider only the octahedral Mn interstitial position.
For the refinement of the lattice structure around the Mn ion in the octahedral interstitial site, we have fitted the measured \( \chi(k) \) EXAFS spectra, using the Artemis (IFEFFIT) software package \[28\]. In the fit we have included six Te atoms in the first coordination shell and two Bi atoms in the second coordination shell. The measured and fitted \( \chi_k \) and \( \chi_R \) curves of samples with \( x_{\text{Mn}} = 4, 6, 9, 13\% \) are displayed in figures 8(a) and (b). From these fits, the NN and next-nearest neighbor (NNN) distances \( -d_{\text{Mn-Te}} \) and \( -d_{\text{Mn-Bi}} \) are obtained and the results are listed in table 3. We obtained \( d_{\text{Mn-Te}} \approx 0.291 \text{ nm} \) and \( d_{\text{Mn-Bi}} \approx 0.303 \text{ nm} \) for all samples, with an insignificant variation in dependence of the Mn content. This value is very close to the nominal value expected for undistorted pure \( \text{Bi}_2\text{Te}_3 \), whereas for the other possible incorporation sites, much different values would be expected (see table 1). The low Mn concentration for the \( x_{\text{Mn}} = 4\% \) sample and the resulting comparatively high noise level in the data, did not allow us to fit the positions of the Bi atoms in the second coordination shell, i.e., only the Te positions in the first shell were refined for this sample.

We note that for the samples with low Mn contents of \( x_{\text{Mn}} = 4 \) and 6\%, the theoretical \( \chi(R) \) curves differ significantly in the range \( R < 0.15 \text{ nm} \). This region corresponds to long-range oscillations in energy dependence of the absorption spectrum \( \mu(E) \), which is very sensitive to method used for the background subtraction. Since the measured fluorescence signal is proportional to the Mn content, the background and signal-to-noise is how it’s usually stated ratio is higher for the samples with lower Mn content compared to those obtained for high \( x_{\text{Mn}} \). The error limits in table 3 were determined as the reproducibility of the fitted distances with respect to various normalization methods of \( \chi(R) \) obtained by the several data normalization methods available by the Athena software. The fitted \( d_{\text{Mn-Te}} \) values correspond within the error limits to the expected theoretical value of the ideal \( \text{Bi}_2\text{Te}_3 \) lattice listed in table 1. On the other hand, from the XRD data, we found that increasing the Mn concentration induces a contraction of the averaged lattice, both in lateral and vertical directions, which should affect the \( d_{\text{Mn-Te}} \) distances determined by EXAFS. However, the error limits of the EXAFS data are much larger than error limits of the XRD data, i.e., they are as large as the XRD observed-lattice contraction. Therefore, the sensitivity of EXAFS data does not allow us to see the effect of the small average lattice contraction to the first coordination around interstitial Mn atoms that was deduced by x-ray diffraction.

Table 3. Distances of the six nearest tellurium atoms and two nearest bismuth atoms to the central Mn atom in octahedral configuration in Mn-doped bismuth telluride with different Mn concentrations \( x_{\text{Mn}} = 0 \) to 13\% as determined from the fit of the \( \chi(R) \) EXAFS data using the model of Mn incorporated interstitially in octahedral positions in the vdW Te–Te gap.

| \( x_{\text{Mn}} \) (%) | \( d_{\text{Mn-Te}} \) (nm) | \( d_{\text{Mn-Bi}} \) (nm) |
|-----------------|-----------------|-----------------|
| 4               | 0.290 ± 0.009   | —               |
| 6               | 0.292 ± 0.004   | 0.304 ± 0.010   |
| 9               | 0.292 ± 0.004   | 0.303 ± 0.010   |
| 13              | 0.291 ± 0.006   | 0.306 ± 0.014   |

For the refinement of the lattice structure around the Mn ion in the octahedral interstitial site, we have fitted the measured \( \chi(k) \) EXAFS spectra, using the Artemis (IFEFFIT) software package \[28\]. In the fit we have included six Te atoms in the first coordination shell and two Bi atoms in the second coordination shell. The measured and fitted \( \chi(k) \) and \( \chi(R) \) curves of samples with \( x_{\text{Mn}} = 4, 6, 9, 13\% \) are displayed in figures 8(a) and (b). From these fits, the NN and next-nearest neighbor (NNN) distances \( d_{\text{Mn-Te}} \) and \( d_{\text{Mn-Bi}} \) are obtained and the results are listed in table 3. We obtained \( d_{\text{Mn-Te}} \approx 0.291 \text{ nm} \) and \( d_{\text{Mn-Bi}} \approx 0.303 \text{ nm} \) for all samples, with an insignificant variation in dependence of the Mn content. This value is very close to the nominal value expected for undistorted pure \( \text{Bi}_2\text{Te}_3 \), whereas for the other possible incorporation sites, much different values would be expected (see table 1). The low Mn concentration for the \( x_{\text{Mn}} = 4\% \) sample and the resulting comparatively high noise level in the data, did not allow us to fit the positions of the Bi atoms in the second coordination shell, i.e., only the Te positions in the first shell were refined for this sample.

We note that for the samples with low Mn contents of \( x_{\text{Mn}} = 4 \) and 6\%, the theoretical \( \chi(R) \) curves differ significantly in the range \( R < 0.15 \text{ nm} \). This region corresponds to long-range oscillations in energy dependence of the absorption spectrum \( \mu(E) \), which is very sensitive to method used for the background subtraction. Since the measured fluorescence signal is proportional to the Mn content, the background and signal-to-noise is how it’s usually stated ratio is higher for the samples with lower Mn content compared to those obtained for high \( x_{\text{Mn}} \). The error limits in table 3 were determined as the reproducibility of the fitted distances with respect to various normalization methods of \( \chi(R) \) obtained by the several data normalization methods available by the Athena software. The fitted \( d_{\text{Mn-Te}} \) values correspond within the error limits to the expected theoretical value of the ideal \( \text{Bi}_2\text{Te}_3 \) lattice listed in table 1. On the other hand, from the XRD data, we found that increasing the Mn concentration induces a contraction of the averaged lattice, both in lateral and vertical directions, which should affect the \( d_{\text{Mn-Te}} \) distances determined by EXAFS. However, the error limits of the EXAFS data are much larger than error limits of the XRD data, i.e., they are as large as the XRD observed-lattice contraction. Therefore, the sensitivity of EXAFS data does not allow us to see the effect of the small average lattice contraction to the first coordination around interstitial Mn atoms that was deduced by x-ray diffraction.

In \[15\], it has been suggested that Mn induces the creation of excess Bi–Bi double layers into which Mn atoms are substitutionally incorporated. According to this work, when increasing the Mn content, the structure
should change from pure Bi$_2$Te$_3$ phase towards the Bi$_2$Te$_5$ phase, in which a Bi–Bi DL occurs periodically after each pair of Te–Bi–Te–Bi–Te QLs. In our previous work [19], the structure of various Bi$_2$Te$_{3-x}$ phases was studied in detail, revealing that with increasing $\delta$, i.e., when moving from Bi$_2$Te$_3$ towards Bi$_2$Te$_5$, the in-plane lattice parameter $a$ increases, whereas the vertical lattice parameter $c$ decreases. This is in contradiction to our results observed for Mn-doped Bi$_2$Te$_2$, where both lattice parameters $a$ and $c$ decrease with increasing $x_{\text{Mn}}$ (see figure 3 and table 2). This fact supports our conclusion that the Mn atoms occupy interstitial places and do not evoke the creation of Bi–Bi DLs.

Finally, we compare the positions of the Te atoms in the first coordination shell around octahedral Mn interstitials in the vdW gaps with those of the Te atoms surrounding Mn in cubic MnTe$_2$ [24] [figures 1(d) and (e)]. We find that the structure of both first coordination shells, as well as the NN distances, is very similar indeed. Thus, the local lattice configuration around an occupied octahedral Mn interstitial can be considered as slightly deformed MnTe$_2$. This similarity is also obvious from the comparison of the measured and simulated EXAFS spectra in figure 7, where the spectrum simulated for the pyrite MnTe$_2$ is quite close to the experimental data for larger energies, i.e., for larger lengths of the photoelectron wave vector $k$. This coincidence implies the similarity of the first coordination shell around Mn in the investigated samples and in MnTe$_2$.

As the origin for the additional modulation of the lattice along the growth direction [0001] with the period of $L_{\text{mod}} \approx 2D$, we propose that the Mn-occupation of the adjacent vdW gaps is not statistically independent, and a self-organized Mn modulation wave is created. This hypothesis needs further investigation. We note that if the Mn ions exclusively occupy octahedral positions and these sites occur on average only in every $m$th vdW Te–Te gap, the full occupation of these places corresponds to the phase Mn$_{1/n}$Bi$_2$Te$_3$. From this, it follows that in samples with $x_{\text{Mn}} = 13\%$ and $m = 2$, every fourth of the possible octahedral sites within the vdW gaps is occupied.

6. Summary

Structural investigations of epitaxial ferromagnetic layers of the Mn-doped topological insulator Bi$_2$Te$_3$ reveal that the Mn dopant ions are incorporated mostly in octahedral interstitial positions in the middle of the van der Waals gaps between the adjacent Te layers of the quintuple layers. The local environment of the Mn ions corresponds to a distorted cubic MnTe$_2$ lattice with a nearest neighbor Mn–Te distance of 0.2901 Å. From the EXAFS data, we can rule out that Mn resides in sizable amounts on substitutional Bi sites or on tetrahedrally coordinated interstitial sites. This explains the rather small effect of Mn on the carrier type and concentration of the samples. These findings provide an important input for the ongoing experimental and theoretical investigations on the mechanisms that mediate ferromagnetism in $n$-type transition-metal-doped topological insulators in which charge carriers do not seem to play any dominant role, unlike in conventional Mn-doped ferromagnetic III–V semiconductors. Moreover, our findings are important for theoretical modeling of the effect of Mn incorporation on the topological surface state of bismuth telluride.

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