Study of the structural, electric and magnetic properties of Mn-doped Bi$_2$Te$_3$ single crystals

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Abstract. Breaking the time reversal symmetry of a topological insulator, for example by the presence of magnetic ions, is a prerequisite for spin-based electronic applications in the future. In this regard Mn-doped Bi$_2$Te$_3$ is a prototypical example that merits a systematic investigation of its magnetic properties. Unfortunately, Mn doping is challenging in many host materials—resulting in structural or chemical inhomogeneities affecting the magnetic properties. Here, we present a systematic study of the structural, magnetic and magnetotransport properties of Mn-doped Bi$_2$Te$_3$ single crystals using complimentary experimental techniques. These materials exhibit a

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ferromagnetic phase that is very sensitive to the structural details, with $T_C$ varying between 9 and 13 K (bulk values) and a saturation moment that reaches $4.4(5) \mu_B$ per Mn in the ordered phase. Muon spin rotation suggests that the magnetism is homogeneous throughout the sample. Furthermore, torque measurements in fields up to 33 T reveal an easy axis magnetic anisotropy perpendicular to the ab-plane. The electrical transport data show an anomaly around $T_C$ that is easily suppressed by an applied magnetic field, and also anisotropic behavior due to the spin-dependent scattering in relation to the alignment of the Mn magnetic moment. Hall measurements on different crystals established that these systems are n-doped with carrier concentrations of $\sim 0.5-3.0 \times 10^{20} \text{cm}^{-3}$. X-ray magnetic circular dichroism (XMCD) at the Mn $L_{2,3}$ edge at 1.8 K reveals a large spin magnetic moment of $4.3(3) \mu_B$/Mn, and a small orbital magnetic moment of $0.18(2) \mu_B$/Mn. The results also indicate a ground state of mixed d$^4$–d$^5$–d$^6$ character of a localized electronic nature, similar to the diluted ferromagnetic semiconductor Ga$_{1-x}$Mn$_x$As. XMCD measurements in a field of 6 T give a transition point at $T \approx 16$ K, which is ascribed to short range magnetic order induced by the magnetic field. In the ferromagnetic state the easy direction of magnetization is along the c-axis, in agreement with bulk magnetization measurements. This could lead to gap opening at the Dirac point, providing a means to control the surface electric transport, which is of great importance for applications.

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1. Introduction

Interest in Bi$_2$Te$_3$ and related materials systems has recently been revived with the observation of topologically protected surface states [1]. The edge state of a topological insulator (TI) is protected by time reversal symmetry, so that the electrical conduction is robust against backscattering. Among the most studied systems, Bi$_2$Te$_3$ exhibits no magnetic ordering and single crystals are typically p-type semiconductors that can become superconducting under pressure [2]. However, doping Bi$_2$Te$_3$ with transition metal ions such as Fe [3] or Mn [4–6]
can lead to the formation of ferromagnetic order. A ferromagnetic state has also been reported for related systems such as V-doped Sb$_2$Te$_3$ [7] and Cr-doped (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ [8]. On the other hand, intercalating Cu into Bi$_2$Se$_3$ induces a bulk superconducting state [9], which may host Majorana fermions [10].

Transition metal doping of semiconductors is an active field of research, as magnetic semiconductors such as Mn-doped GaAs [11], Ge [12, 13] and Si [14] are a prerequisite for spintronics applications, in which both the spin and the charge of the electron are exploited for information processing [15]. The main goal of achieving room-temperature ferromagnetism in homogeneous (i.e. segregation-free) versions of these materials has proven difficult to achieve. One of the challenges is the synthesis of doped, homogeneous crystals. So far, even nominally identically prepared samples show a diversity of magnetic transition temperatures, saturation magnetizations, and anisotropies—indeed these properties can vary even over the extend of a single crystal. Mn-doped Bi$_2$Te$_3$ and related compounds are no exception. More importantly, the layered crystal structure of these materials allows the dopants not only to enter the host substitutionally or interstitially, but also in the van der Waals gap between the layers.

Further, for the realization of the topological properties in these materials their bulk electronic properties have to be controlled by finding ways to reduce the defect densities, and by understanding the role of dopants and intercalated ions. One of the first studies to show the interplay between ferromagnetism and the breaking of time reversal symmetry in a TI was reported by Hor et al [6] in Mn-doped Bi$_2$Te$_3$. They found that ferromagnetic order is established for Mn concentrations higher than $x = 0.04$ in Mn$_x$Bi$_{2-x}$Te$_3$, with a Curie temperature ($T_C$) varying between $\sim 9$ and 12 K. Angle resolved photoemission spectroscopy (ARPES) of the surface state has shown a gap opening at the Dirac point due to the presence of magnetic impurities [16].

This paper reports a study of Mn-doped Bi$_2$Te$_3$ single crystals with nominal Mn concentrations of $x_n = 0.09$ and 0.15. These show a ferromagnetic transition temperature of $\sim 9–13$ K with clear signatures of a phase transition in magnetic and magnetotransport measurements. A combination of structural, electrical and bulk and surface sensitive magnetic probes, such as superconducting quantum interference device (SQUID) and torque magnetometry, muon spin rotation ($\mu$SR) and x-ray magnetic circular dichroism (XMCD), are employed to obtain an insight into the doping of TIs, studying the link between the structural details and the physical properties.

2. Structural analysis

Mn-doped Bi$_2$Te$_3$ single crystals, typically measuring 2–3 cm in length and 1 cm in diameter, were grown using high purity (>99.99%) Bi, Te and Mn. Stoichiometric amounts of the constituent materials, according to Mn$_x$Bi$_{2-y}$Te$_3$ with nominal Mn concentrations of $x_n = 0.09$ and 0.15, were mixed, sealed in an evacuated quartz ampoule, and then heated to a temperature of 1003 °C over 24 h. After 10 h at this temperature, they were cooled down to 855 °C at the rate of 10 °C h$^{-1}$. The actual crystal growth occurred during the cooling of the melt from 855 to 529 °C at the rate of 5 °C h$^{-1}$. Finally, the crystals were annealed at 529 °C ($x_n = 0.09$) and 579 °C ($x_n = 0.15$) for 80 h and then cooled to room temperature at the rate of 10 °C h$^{-1}$. It has to be noted that the melting point increases with Mn concentration. Hereafter the samples are referred to according to their nominal Mn composition, $x_n$. The off-stoichiometry of Bi, denoted $(2 - y)$, is addressed below.
The single crystals were analyzed by x-ray diffraction (XRD) at room temperature using a SuperNova Oxford Diffraction system, confirming the $\text{Bi}_2\text{Te}_3$ crystal structure with space group $R\overline{3}m$ (cf figure 1). The calculated lattice parameters show very little variation with doping concentration: $a = 4.39(2)\,\text{Å}$ and $c = 30.35(15)\,\text{Å}$ for $x = 0.09$, and $a = 4.386(6)\,\text{Å}$ and $c = 30.42(10)\,\text{Å}$ for $x = 0.15$, respectively. They are almost identical to the ones obtained for undoped samples ($a = 4.384\,\text{Å}$ and $c = 30.45\,\text{Å}$). The cleavage plane is the $ab$-plane, which is perpendicular to the hexagonal $c$-axis. Stacking faults are common due to the layered crystal structure of these very soft materials with only weak van der Waals forces between the quintuple layers [17], which also makes reproducible cleaving or exfoliation difficult. Some disorder is always observed in the $(h0l)$ and $(0kl)$ planes, whereas the $(hk0)$ plane is always cleaner, as seen in figure 1.

Electron probe microanalysis with wavelength-dispersive x-ray spectroscopy and energy-dispersive x-ray spectroscopy (EDX) were performed to determine the materials composition of the samples. Extensive EDX analysis from over 30 points taken from different regions on each sample is shown in figure 2, and indicates that the samples with nominal Mn concentrations of $x = 0.09$ and 0.15 have similar average Mn doping concentrations. The statistical error for the Mn concentration is $\sim0.01$ and for Bi $\sim0.02$. EPMA analysis, which typically gives more accurate quantitative compositional information, was carried out on fewer sites but gave very similar chemical compositions of $\text{Mn}_{0.10}\text{Bi}_{1.98}\text{Te}_3$ for $x = 0.09$ and $\text{Mn}_{0.09}\text{Bi}_{2.00}\text{Te}_3$ for $x = 0.15$.

The compositional analysis by EDX (figure 2) reveals a large scatter of the data, which is more pronounced in both Bi and Mn concentration for the $x = 0.09$ sample, which was annealed at a lower temperature. For clarity, two compositional scenarios are indicated by...
Figure 2. Compositional analysis of Mn-doped Bi$_2$Te$_3$ crystals obtained on various cleaved pieces and several spots for nominal Mn doping concentrations of $x_n = 0.09$ (red dots) and $x_n = 0.15$ (blue triangles). The solid line represents a fixed Bi:Te stoichiometry of 2:3 with Mn being incorporated interstitially; the dashed line a (substitutional) Mn incorporation according to Mn$_x$Bi$_{2-x}$Te$_3$. The undoped sample data is indicated by black squares. The gray shaded area represents the approximate range of the solubility limit of $x = 0.11(1)$.

Figure 3. Bright-field TEM images for crystals with nominal compositions: (a) $x_n = 0.09$ and (b) $x_n = 0.15$. Diffraction contrast from the strain fields surrounding the Mn-rich precipitates is visible only for the high Mn content in (b).

straight lines: the ‘interstitial’ compound Mn$_x$Bi$_2$Te$_3$ by a solid line and the ‘substitutional’ compound Mn$_x$Bi$_{2-x}$Te$_3$ by a dashed line. For $x_n = 0.15$, the compositional data is found within the two bounding lines, with a Bi concentration of slightly below 2. For the lower doping concentration ($x_n = 0.09$), the spread in both Bi and Mn concentration is much larger, however, there is a trend toward the Mn$_x$Bi$_{2-x}$Te$_3$ line. Figure 2 suggests that the maximum solubility of Mn in the growing Bi$_2$Te$_3$ crystals is $x_{\text{lim}} = 0.11(1)$ (indicated by the shaded area).

Transmission electron microscopy (TEM) shows the presence of nm-scale Mn-rich precipitates in the $x_n = 0.15$ crystal (see figure 3(b)), whereas the $x_n = 0.09$ crystal (see in figure 3(a)) does not show any evidence of precipitation. This suggests that Mn incorporates in solid solution in the $x_n = 0.09$ sample but as the concentration of Mn in the melt is increased,
supersaturation occurs in the crystal during cooling, supporting the hypothesis of a solution limit no larger than \( x_{\text{lim}} = 0.11 \).

In addition, high-resolution electron-back-scatter diffraction analysis was performed; this technique uses image correlation techniques to measure spatial variations in lattice parameters with very high precision [18]. The results clearly show a quasi-periodic \( \mu \text{m-scale} \) variation in \( c/a \) ratio in the \( x_n = 0.09 \) crystal, whereas (for the given spatial resolution) the \( x_n = 0.15 \) crystal is found to be more homogeneous (see figure 4). This interesting microstructure is thought to develop as a result of the internal stresses in the material produced by the Mn substitution, and may be a result of the local compositional variations suggested by the EDX results.

3. Magnetic characterization

The magnetic properties of Mn-doped Bi\(_2\)Te\(_3\) were studied by a combination of complementary magnetic measurement techniques which are sensitive to the bulk, ‘thin film’ and surface properties. While SQUID and torque magnetometry, as well as \( \mu \)SR and magnetotransport give access to bulk properties, XMCD is mostly sensitive to the surface and near-surface areas of the materials.

3.1. Magnetization measurements

SQUID magnetometry was performed as a function of temperature and magnetic field, in different orientations with respect to the \( ab\)-plane, using a 7 T quantum design magnetic properties measurement system, with results shown in figure 5. The hysteresis loops measured on \( x_n = 0.15 \) crystals show that the samples are soft ferromagnets with small coercive fields of \( \sim 70 \text{ mT} \) at 1.8 K (for \( H \parallel c \)), as shown in figure 5(a), with a saturation magnetic moment of 4.4(5) \( \mu_B \) per Mn atom reached at \( \sim 1.5 \text{ T} \). Magnetization measurements on the \( x_n = 0.09 \) batch, shown in figure 5(c), reveal a more complex low temperature hysteresis with a characteristic double-step behavior. The first plateau reaches 3.5(4) \( \mu_B \), while the saturation moment is 5.0(5) \( \mu_B/\text{Mn} \). The stated error is largely due to the uncertainty in composition.
Figure 5. Magnetization measurements of Mn-doped Bi$_2$Te$_3$ single crystals. (a) Magnetization loops of a $x_n = 0.15$ crystal with the magnetic field parallel to the hexagonal $c$-axis with a saturation moment of 4.5(4) $\mu_B$/Mn at 1.8 K. (b) Magnetic hysteresis loops obtained with the field perpendicular and parallel to the $ab$-plane, showing an easy axis of magnetization perpendicular to the $ab$-plane. (c) Magnetic hysteresis loop of a $x_n = 0.09$ crystal at 1.8 and 5 K. The 1.8 K data shows a very pronounced double step structure, saturating at a value of 5.0(5) $\mu_B$/Mn. (d) Magnetization measurements as a function of applied field for a crystal with $x_n = 0.09$ showing similar anisotropy properties to the $x_n = 0.15$ sample. (e) Arrott plot analysis [19]; by extrapolation from high field data, $T_C$ is found to be between 9 and 10 K for $x_n = 0.15$. For the scaling of the data it is assumed that Mn enters the crystal according to Mn$_{0.9}$Bi$_2$−$x_{\text{exp}}$Te$_3$ using the experimental Mn concentrations from EPMA measurements. (f) Inverse magnetic susceptibility as a function of temperature for $x_n = 0.15$; the solid line is a fit to the Curie–Weiss law in the paramagnetic phase, as discussed in the text.

The measured saturation magnetization of 4.4(5) $\mu_B$/Mn is found to be between the expected value for high spin Mn$^{3+}$ (4 $\mu_B$) and Mn$^{2+}$ (5 $\mu_B$). It is consistent with calculations which give 4 $\mu_B$ [20] and 4.5 $\mu_B$ [21], respectively. However, our results disagree with previous reports on $x = 0.09$ samples that give a saturation value of 1.5 $\mu_B$/Mn [6]. Further, steps are observed in the magnetization curve for the easy axis loop for $x_n = 0.09$ (figure 5(c); as well as in the XMCD measurements shown in figure 10(c)). A similar step structure has been observed in other diluted magnetic semiconductors (DMSs), such as Mn-doped II–VI materials [11].

An effective moment of 5.1(5) $\mu_B$/Mn atom (for $H \parallel ab$) is extracted from the high temperature susceptibility data using the Curie–Weiss law as shown in figure 5(f), larger than the $\sim$4 $\mu_B$/Mn atom reported in [6]. This value again lies between the expected effective moments for Mn$^{3+}$ and Mn$^{3+}$ assuming only a spin contribution. For Mn$^{3+}$, $p_{\text{eff}} = 2\sqrt{3(S+1)}$ is 4.9 and 5.9 $\mu_B$/Mn for Mn$^{2+}$. A substantial reduction of the saturated moment compared to the paramagnetic moment is therefore not observed, as it was in [6], where it was attributed to the effects associated with itinerant ferromagnetism. Discrepancies between predicted and
Figure 6. Magnetic torque measurements on a $x_n = 0.09$ crystal. (a) Torque versus magnetic field data for different orientations at 0.35 K. The peak features around 1–2 T arise from a rotation of the magnetization due to the applied magnetic field at an angle $\theta$ away from the easy axis $c$-axis (where $\theta = 0^\circ$ for $H||c$). (b) Simulated torque assuming a Landau model ferromagnet with uniaxial anisotropy, as described in the text. (c) The theoretical curves for a uniaxial crystal, as proposed in [24], reduce to a straight line for $\theta = 45^\circ$ (dashed line). (d) The anisotropy constant can be derived from the experimental data near $\theta = 45^\circ$ as discussed in the text.

measured values of the moment have been reported in thin films of Ga$_{1-x}$Mn$_x$As as well, with 4 and 4.5 $\mu_B$/Mn for defect-free and interstitial Mn samples, respectively [22].

The transition temperature $T_C$ can be determined using Arrott’s method [19], as shown in figure 5(e). Following a Landau approach, above any hysteresis limits, the magnetization takes the form $H/M = a'(T - T_C) + b'M^2 + c'M^4$. The sign of the intercept changes at $T_C$ allowing for it to be determined from isothermal field sweeps. The straight-line fits to the high field data give an extrapolated value $T_C \approx 9.4$ K consistent with $T_C = 9.3$ K estimated from the resistivity in $x_n = 0.15$ (as discussed in section 3.4).

The hysteresis loops recorded with the field perpendicular to and in the $ab$-plane (figure 5(b)) display a uniaxial anisotropy with the $c$-axis being the easy axis and a magnetic anisotropy of $K_1 = 11$ kJ m$^{-3}$ (for the $x_n = 0.15$ sample as determined from figure 5(a) in conjunction with the hard axis loop (not shown) using $K_{\text{eff}} = \int_0^M \mu_0H \, dM$). This can be compared with a magnetocrystalline anisotropy constant of $\sim$3 kJ m$^{-3}$ in Mn$_x$Ga$_{1-x}$As [23], which has a doping dependent $T_C$ an order of magnitude larger than Mn-doped Bi$_{2-x}$Te$_3$.

3.2. Magnetic torque

The anisotropy of the $x_n = 0.09$ crystals was determined independently through magnetic torque measurements at 0.35 K in fields up to 33 T, as shown in figure 6(a). Torque, resulting from the tendency of the sample to align in the magnetic field, is measured using piezoresistive microcantilevers [25]. The crystals typically measure $100 \times 100 \times 20 \mu$m$^3$ and are fixed to the cantilevers using Apiezon-N grease, which freezes at low temperature. The cantilever is
placed on a rotating probe in a helium-3 cryostat inside of the 33 T magnet at the High Field Magnetic Laboratory in Nijmegen, Netherlands. The torque signal depends on the anisotropy of the system: for an easy axis magnet the magnetization is aligned approximately along the easy axis at low fields, and parallel to the field direction at high fields. In our measurements on Mn-doped Bi$_2$Te$_3$ the easy axis of magnetization is along the $c$-axis (see also magnetization measurements in section 3.1) and the anisotropy leads to low field features when the angle of the magnetization shifts dramatically.

These low field features can also be qualitatively reproduced in torque simulations using a Landau model for a ferromagnet with uniaxial anisotropy, as shown in figure 6(b). By minimizing the energy, $U = -\mu_0 MVH\cos(\beta - \alpha) + K V \sin^2 \beta$, of a magnetic crystal of volume $V$ in an applied magnetic field $H$, with respect to $\beta$, the angle between the magnetization $M$ and the $c$-axis, the torque can be calculated as

$$\tau = \mu_0 MVH \sin(\beta - \alpha),$$

where $\alpha$ is the angle between the magnetic field, $H$, and the $c$-axis (which is the easy axis of magnetization for $K > 0$). Due to the nature of microcantilever experiments absolute torque values cannot be easily obtained. In a uniaxial material, anisotropy parameters can be obtained by plotting $(\tau/H)^2$ against $\tau$, which takes the form of a straight line in the special case of $\alpha = 45^\circ$, as shown in figure 6(c). This assumes that the absolute value of the saturation magnetization, $M_S$, remains constant [24]. Denoting $\tau_{arb}$ as the measured torque in arbitrary units, $\tau_{SI}$ as the torque in SI units, and the constant $r$ as the conversion factor between these two, Miyajima’s equations for the intercepts ($\tau_\infty$ on the $\tau$-axis) and $C$ on the $(\tau/H)^2$ axis, are $\tau_{arb} = r \tau_{SI} = r K V$ and $C_{arb} = r^2 C_{SI} = \frac{1}{2} (MV)^2$. Combining the two yields $r K V / r M V = K / M = \tau_{arb}/\sqrt{2C_{arb}} = 0.718$. Using $M_S = 4.4 \mu_B$/Mn, obtained from magnetization measurements of the $n = 0.15$ sample (see figure 5), results in a quantitative value for the anisotropy of Mn-doped Bi$_2$Te$_3$ of $K = 0.507 M_S = 11 kJ m^{-3}$, which is in perfect agreement with the value obtained from the magnetic hysteresis loops.

3.3. Muon spin rotation

Bulk $\mu$SR experiments were performed at the ISIS pulsed neutron and muon facility on the instrument EMU. Muons are spin-$\frac{1}{2}$ particles that are sensitive to their local magnetic environment. $\mu$SR is well suited to the exploration of local magnetic correlations as the spatial sensitivity of the probe decreases rapidly, giving an effective sampling radius of 20 Å. The energy of the incident muons (4 MeV) gives a bulk implantation depth of $\sim 0.5$ mm and allows for an estimation of the magnetic volume fraction of the sample. The spin of the muon is antiparallel to the incoming momentum. Therefore, homogeneous internal fields with respect to the muon stopping site lying off this axis give rise to oscillating spectra with respect to the symmetrical detectors in zero field [26]. When the internal field is larger than $\sim 60$ mT the oscillations can no longer be resolved at the ISIS pulsed source and the fast frequency results in a missing asymmetry fraction, whereas any ordered moments aligned along the muon polarization axis result in an observable non-relaxing tail. For Mn-doped Bi$_2$Te$_3$ in zero field there is a missing asymmetry below $T_C$ due to a large internal field resulting from a precession frequency which is too fast to be resolved at the ISIS pulsed source. This is in contrast to Fe-doped Bi$_2$Se$_3$, which has a lower internal field at the muon stopping site [27]. However, weak transverse field (with respect to the muon spin) experiments can be performed which allow for the calculation of the magnetic volume fraction.
Figure 7. $\mu$SR measurements on Mn-doped Bi$_2$Te$_3$. (a) Total asymmetry plotted as a function of time for the $x_n = 0.15$ sample. The solid red lines are fits to the data as described in the text. (b) The amplitude $A_1$ of the oscillating component in equation (2), as a function of temperature for both the $x_n = 0.15$ and 0.09 sample. The horizontal red (drawn) line represents the signal from the hematite backing plate. $A_1$ drops down to the background level which suggests that the full volume fraction of both samples is magnetically ordered.

Samples were mounted by nominally aligning the crystals in a mosaic with their $c$-axis along the direction of the incoming muon spin on a hematite backing plate. In the temperature range of interest hematite is an ordered magnet with internal fields too large to be resolved. Therefore, when a transverse field is applied only a flat background is observed. Figure 7(a) shows the spectra for the $x_n = 0.15$ sample at 20 and 2.3 K, above and below $T_C$, respectively. The spectra can be fitted with a function of the form

$$A(t) = A_1 \exp(-\lambda_i t) \cos(2\pi \nu_i t) + A_{NO},$$

(2)

where $A_1$ represents the relative contribution for those muons undergoing coherent precession, $A_{NO}$ is the non-precessing signal amplitude due to a local field distribution parallel to the initial spin polarization of the muon, $\lambda$ is the relaxation rate and the frequency of the oscillations, $\nu_i$ can be expressed by $\nu_i = \gamma_\mu |B_i|/2\pi$, where $B_i$ is the average magnitude of the local field at the $i$th muon site and $\gamma_\mu$ is the muon gyromagnetic ratio. Above $T_C$ the signal is a composition of muons stopping in the sample and a small background component of muons stopping in the cryostat tails (not in the hematite backing plate). However, below $T_C$, $A_{NO}$ increases as the applied field of 2 mT is smaller than the randomly oriented internal static fields (>60 mT), which may have a component along the direction of the incoming muon spin, and the only oscillating component is from the instrument background, i.e. muons stopping in the cryostat tail. To confirm this, measurements were performed with only the hematite backing plate and the amplitude of the oscillating component is shown in figure 7(b) as a horizontal red line. Figure 7(b) shows the temperature dependence of $A_1$ for both the $x_n = 0.09$ and 0.15 Mn concentrations. In both cases the signal from the sample vanishes below $T_C$, suggesting a full volume fraction of magnetization. The difference in the initial asymmetry between the two samples above $T_C$ is simply a consequence of the amount of sample material used, with the $x_n = 0.09$ sample having a smaller stopping area. Fitting a critical type behavior to both $\lambda$ and $A_{NO}$ gives an estimation of $T_C \approx 9.5$ K for both samples, in good agreement with the bulk electrical and magnetization measurements.
3.4. Magnetotransport measurements

Magnetotransport and Hall effect measurements were performed on single crystals of Mn-doped Bi$_2$Te$_3$ using an ac transport technique in standard four-point probe and Hall geometries with the current flowing in the $ab$-plane. These measurements were done as a function of temperature and magnetic field using a 14 T Quantum Design PPMS system.

In zero field, the temperature dependence of resistivity shows a metallic behavior, with a low residual resistivity ratio of $\sim 2–3$ and a base resistivity of $\sim 0.3$ m$\Omega$ cm, both indicative of the disorder introduced by the Mn dopants. Cooling through the transition produces a distinct anomaly shown in figure 8(b). In similar systems [7, 28] the maximum of the zero field
The resistivity anomaly is taken to be an estimate of $T_C$—in this case giving $T_\rho = 9.3$ K from where $d\rho/dT$ passes through zero. Among the different samples measured some variation is found in both the magnitude and the position of the resistivity peak with $T_C$ varying between 9 and 13 K, as seen in figure 8(a).

The resistivity anomaly has been observed in several related compounds, e.g. Mn-doped GaAs (29), V-doped Sb$_2$Te$_3$ (7) and indeed in p-type Mn-doped Bi$_2$Te$_3$ [4, 6]. It can be explained by an increase in carrier scattering near $T_C$ due to exchange interaction with spin fluctuations. The peak is suppressed and moves to higher temperatures under the application of a small magnetic field oriented perpendicular to the $ab$-plane (figure 8(c)). Magnetoresistance data (figure 8(d)) show a low field negative behavior superimposed on the typical magnetoresistive parabolic ($\sim B^2$) dependence, with a maximum resistivity suppression of $\Delta \rho / \rho = 4.5\%$ at 1.9 T and 9 K. At temperatures much higher than $T_C$ the usual parabolic dependence is observed. The negative magnetoresistive effect is most prominent at $T_C$, but persists up to temperatures significantly above $T_C$. It originates from the reduction of spin-dependent scattering due to the alignment of local magnetic spins [30]. Since around $T_C$ these fluctuations are at a maximum, the negative magnetoresistance is most pronounced at these temperatures.

At low temperatures, the resistivity shows a hysteretic behavior (see figures 8(e)–(g)). For $H || c$ the magnetoresistive dip discussed earlier is observed. The maximum resistance, $\rho_{\text{max}}$, is found at $\pm 70$ mT (see figure 8(e)). This corresponds approximately to the coercivity field value. When the net sample magnetization is zero, the scattering is maximized. With an increase in temperature, hysteretic effects become suppressed (see figure 8(g)). In a different geometry with the field aligned parallel to the current path (see figure 8(f)), similar negative magnetoresistance phenomena are observed due to the alignment of the spins, although in this case the alignment is not along the easy axis of the crystal but along the field, and $\rho_{\text{max}}$ is found at a higher field.

Hall measurements, shown in figure 8(h), demonstrate that the samples are n-type, with carrier densities in the range of $\sim 0.5$–3.0 $\times 10^{20}$ cm$^{-3}$, which is comparable to the nominal Mn density of $N_{\text{Mn}} = 5.3 \times 10^{20}$ cm$^{-3}$ for $x_n = 0.09$. Below $T_C$, the anomalous Hall effect is observed, indicating spin polarization of the charge carriers. The magnitudes of the anomalous and ordinary Hall coefficients are comparable (ratio of $\sim 2.2$ at 2 K); the first term originates from the spin-split bands that give rise to a non-zero $xy$-component which is proportional to the magnetization. On the other hand, the ordinary Hall resistance, which is proportional to the magnetic field, arises, within the simple single-band model, from intra-band transitions between adjacent Landau levels. Beyond the hysteretic behavior, a linear signal is observed up to a field of 14 T (not shown). At higher temperatures this linear signal is almost independent of temperature.

3.5. X-ray magnetic circular dichroism

3.5.1. Spectral features at the Mn L$_{2,3}$ edge. The element-specific technique of XMCD is used to probe the local electronic character of the magnetic ground state [31]. This technique is capable of an unambiguous determination of the electronic and magnetic state of magnetic dopants in TIs [32–36].

X-ray absorption spectra (XAS) of $x_n = 0.09$ samples were obtained in the temperature range from 1.8 to 200 K on beamline I06 at Diamond Light Source using a superconducting magnet capable of applying fields up to 6 T along the direction of the incident x-ray beam [35]. The degree of circular polarization of the x-ray beam delivered in the energy region of interest
is close to 100%, and the spot size of the beam is typically $20 \times 200 \, \mu m^2$, much smaller than the area of the crystal surfaces. XAS measurements were made in total-electron-yield (TEY) mode, which is surface sensitive (with an exponentially decaying sampling depth of 3–5 nm). Clean sample surfaces were obtained by in situ cleaving under ultrahigh vacuum conditions ($<10^{-10}$ Torr). The XMCD is obtained from the difference between two XAS spectra recorded with x-ray helicity vector and applied magnetic field parallel and antiparallel, respectively.

Figure 9(a) shows the Mn $L_{2,3}$ XAS spectra before and after in situ cleaving measured in a 6 T field at 1.8 K. The surface previously exposed to air displays a distinct multiplet structure that is characteristic of a highly localized ground state [37]. After cleaving of the crystal, the multiplet structure becomes less pronounced and the Mn $L_3$ peak maximum shifts by $\sim 0.5$ eV to lower energy. A similar observation was made for the DMS Ga$_{1-x}$Mn$_x$As, where the energy shift and the different multiplet structure after cleaving indicate that the Mn ground state has a mixed d$^4$, d$^5$ and d$^6$ character [37].

From figure 9 it is clear that the $L_3/(L_3 + L_2)$ branching ratio ($L_3$ and $L_2$ stand here for the integrated peak intensities) is higher than the statistically expected value of 2/3. This is an indication that, to a large extent, the Mn d electrons are localized rather than itinerant [38, 39].

Figure 9(b) shows the corresponding XMCD spectra. The XMCD asymmetry is normalized by taking the background of the XAS spectra equal to 1. For the uncleaved crystal the XMCD resembles the multiplet splitting of the atomic Mn d$^5$ configuration [40]. After cleaving the XMCD becomes more intense and shows a sharper and somewhat different multiplet structure. The XMCD of the cleaved crystal arises from a mixed ground state [39, 41]. The remarkable presence of a small but sharp prepeak has been ascribed to states with uniaxial symmetry. This feature will not be further discussed here [42, 43].

3.5.2. Spin and orbital moments from XMCD. Using the sum rules, the ratio of the orbital to spin magnetic moments can be obtained from the integrated intensities over the $L_3$ and $L_2$ edges of the XMCD spectrum [44]. To extract the spin moment from the XMCD in the case of the Mn $L_{2,3}$ edge, a correction factor has to be applied in order to compensate for the large $jj$-mixing between the 2p$_{3/2}$ and 2p$_{1/2}$ core levels, as described in [41]. The integrated XMCD signal from the cleaved sample shown in figure 9(b) gives, after the mentioned correction, an orbital to spin moment ratio of $m_L/m_S = 0.043$, confirming an expected large spin- and small orbital-magnetic moment. The systematic error is expected to be 10%. In the spin sum rule the modest contribution of the magnetic dipole term, $T_z$, is neglected as it is small for a ground state of predominantly d$^5$ character. Since the derived $m_L$ and $m_S$ have the same sign the spin and orbital moments are parallel, which according to Hund’s third rule means that Mn has a more than half filled d shell.

Alternatively, quantitative information on the local magnetic moment of the Mn can also be obtained by comparing the experimental spectra directly to the results of multiplet calculations. This circumvents complications and ambiguities in the sum rule analysis, particularly when there is a large $jj$-mixing, as in the case of Mn. For an atomic many-electron system, the transitions $3d^n \rightarrow 2p^33d^{n+1}$ are calculated using the multiplet theory, in which spin–orbit and electrostatic interactions are treated on an equal footing [45]. The intra-atomic electrostatic interactions include the 2p–3d and 3d–3d Coulomb and exchange interactions. The wave functions of the initial- and final-state configurations are calculated in intermediate coupling using Cowan’s atomic Hartree–Fock code with relativistic corrections [40, 45–47]. By embedding the multiplet calculations into an Anderson impurity model the hybridization
Figure 9. (a) Mn $L_{2,3}$ XAS and (b) XMCD spectra of uncleaved and \textit{in situ} cleaved Mn-doped Bi$_2$Te$_3$, $x_n = 0.09$, at 1.8 K. The solid and dashed XAS curves correspond to positive and negative magnetic fields, respectively of 6 T perpendicular to the surface. Cleaving of the sample gives a shift of $-0.5$ eV in the photon energy of the Mn $L_3$ peak maximum and changes the multiplet structure in the XAS spectra, while features in the XMCD signal are less affected. The integrated XMCD signal from the cleaved sample is also shown (dashed line). (c) Calculated XAS spectra for Mn with opposite magnetization for 100\% circularly polarized x-rays. (d) Direct comparison of experimental and calculated XMCD normalized to the maximum average XAS.
Figure 10. (a) Mn $L_3$ XMCD in a magnetic field of 6 T for the indicated temperatures. (b) The Mn magnetic moment/atom derived using the Mn $L_3$ XMCD peak asymmetries in (a) as a function of inverse temperature, and directly of the temperature (inset), showing a ferro- to para-magnetic phase transition at $T \approx 16$ K. (c) Hysteretic Mn $L_3$ XMCD recorded at 1.8 K with the field applied normal to the sample and at an angle of 60°. The gap opening of the loops indicates a ferromagnetic order at low temperature, in which the preferred axis of magnetization is normal to the surface. The inset shows ±6 T field scans at 200 and 1.8 K.

can be taken into account using a coherent mixing of different configurations $d^{n-1}k$, $d^n$, $d^{n+1}k^{-1} \ldots$ [48].

Figure 9(c) shows the calculated results for a mixed ground state with 16% $d^4$, 58% $d^5$ and 26% $d^6$ character, which gives as average a total d count of 5.1. Figure 9(d) shows a comparison of the calculated and experimental XMCD, where the magnitudes of the spectra are normalized to the maximum of the average XAS. Compared to the atomic $d^5$ configuration, the Anderson-impurity-model calculation for the mixed state gives an energy shift of $-0.5$ eV. This shift arises from the additional screening due to the increased mobility of the d electrons, in good agreement with the experimentally observed energy shift. The calculation gives a ground state with spin moment of $(4.3 \pm 0.3) \mu_B$/Mn atom and orbital moment of $(0.16 \pm 0.02) \mu_B$/Mn atom. The best agreement between experimentally determined and calculated spectra of the XMCD amplitude is obtained for the Mn being 100% magnetically polarized. The calculated total d electron count of 5.1 (i.e. more than half filled d shell) is consistent with the result derived from the sum rule analysis that spin and orbital moments are parallel (i.e. $m_L/m_S > 0$).

3.5.3. Temperature dependence. Figure 10(a) shows the Mn $L_3$ XMCD measured with an applied field of 6 T at a range of different temperatures. With increasing temperature, the spectral shape of the Mn $L_{2,3}$ XMCD remains the same, and there is no energy shift, which suggests that there is only one kind of magnetic Mn ion present. It is clear that a non-vanishing Mn magnetic moment persists up to temperatures well above 100 K. A recent ARPES, magnetometry, and XMCD study [36] on molecular beam epitaxy grown Mn-doped Bi$_2$Se$_3$ thin films reported ferromagnetic order at $T = 45$ K at zero field after applying a magnetic field of 0.5 T along the surface normal.

The temperature dependence of the magnetic moment obtained from the Mn XMCD asymmetries is shown in the inset of figure 10(b), and for clarity is also plotted as a function of inverse temperature in the main panel. Above $T \approx 16$ K the magnetization shows the typical
temperature dependence for paramagnetic ordering. At the transition around 16 K there is a stark change in slope of the magnetization curve. Decisive evidence for ferromagnetic order at low temperature is provided by the hysteresis curve in figure 10(c) which is measured at 1.8 K (as explained in section 3.5.4).

In the first instance, such a high transition temperature of \( T \approx 16 \) K seems surprising since magnetometry resulted in \( T_C \approx 9–13 \) K (see above). However, as has previously been noted [49], a ferromagnetic material does not transform instantaneously to the paramagnetic state but enters a state between ferromagnetism and paramagnetism over a certain range of temperatures above the Curie temperature (the so-called transition region). In pure ferromagnetic materials this range of temperatures is relatively narrow, whereas in alloys and dilute ferromagnetic materials it is usually considerably broader [50]. Inhomogeneities within the samples must also be considered. This behavior is consistent with the \( \mu\text{SR} \) results which show an onset of loss of asymmetry at temperatures higher than \( T_C \) (figure 7). To define the boundaries of the transition region, in addition to the ferromagnetic Curie point \( \theta_f \), there has been introduced the so-called paramagnetic Curie point \( \theta_p \), which fixes the ‘upper’ boundary of the transition region. The difference, \( \theta_p - \theta_f \), increases with increasing concentration of the non-magnetic elements in the material, which leads to an enhancement in the tail of the spontaneous magnetization.

In the case of a ferromagnetic material near the Curie point an external field causes a strong para-process, resulting in short range ordering of the spins (ferromagnetic ordering) even above the Curie point [49]. Spin density waves have also been claimed to play a role [51]. The magnetic field hinders the phase transition from ferromagnetism to paramagnetism. Therefore, one can strictly only speak of a Curie point in the absence of an applied magnetic field. Approaching the Curie point from the high-temperature side, exchange forces begin to play an important role and become sufficient to establish order at short distances, so regions of parallel spins appear, which are essentially local fluctuations of the magnetic order. Averaged over the entire specimen, however, the number of regions with opposite orientations of the magnetization cancel each other, and therefore the specimen as a whole does not have any spontaneous magnetization above the Curie point. This will be influenced by the presence of an applied field and the magnetic history, as it favors short-range ordering of spins parallel to the applied magnet field. Hence, the observed transition point at \( T = 16 \) K gives the temperature below which an applied field of 6 T induces magnetization. This transition point is necessarily above the Curie point, \( \theta_f \). In order to obtain the Curie point one requires measurements across a wider region of \( H–T \) space [19]. This was not pursued, as the \( T_C \) had already been obtained by magnetotransport measurements, and the results of the XMCD measured in a limited region of the \( H–T \) space are consistent with this result.

### 3.5.4. Hysteresis loops from XMCD.

Sweeping the bias field at the fixed photon energy of the Mn \( L_3 \) absorption peak, an XMCD hysteresis loop can be obtained which reveals the magnetic state of the Mn moments. XAS loops were recorded for both left- and right-circularly polarized x-rays. In figure 10(c), the inset shows XMCD loops recorded in fields up to ±6 T at 200 and 1.8 K. The main panel shows the details of the magnetic reversals for a smaller field range up to ±1 T, recorded for two different orientations of the applied field. The magnetization saturates at \( H \approx 0.2 \) T, and in zero field there is a clear hysteretic opening with finite remanent magnetization. Loops measured with applied field normal and at 60° grazing incidence to the surface show that the preferred magnetization axis is along the surface normal (i.e. along the
crystalline $c$-axis), in agreement with SQUID and torque magnetometry, and consistent with measurements on other magnetically doped tetradymites [7].

The exchange field due to the magnetic dopants acts like an effective field $B$ on the spins of the surface-state Dirac fermions. The Hamiltonian of the massive Dirac model can be written as [52, 53]

$$\mathcal{H} = \hbar v_F (\sigma_x k_y - \sigma_y k_x) + g \mu_B B \cdot \sigma,$$

(3)

where $v_F$ is the Fermi velocity, $k$ is the crystal momentum and $\sigma = \{\sigma_x, \sigma_y, \sigma_z\}$ represents the Pauli matrices, with $x$ and $y$ in the surface plane and $z$ along the normal. The last term represents the Zeeman energy where $g$ is the Landé $g$-factor. An in-plane field, $B_{x,y}$, shifts the Dirac point, so that there is no opening of a gap, despite breaking the time-reversal symmetry. However, an out-of-plane field, $B_z$, leads to the opening of a band gap. The easy-magnetization direction along the $c$-axis observed in Mn doped Bi$_2$Te$_3$ can therefore open a gap—a prerequisite for future applications in electronic devices.

4. Discussion

Our samples display n-type doping, from which it can be inferred that Mn enters the Bi$_2$Te$_3$ host interstitially, at least to some degree. This is because interstitial Mn acts as a donor. In contrast, Mn that is substitutional on Bi sites lowers the chemical potential and leads to p-type conduction [6]. This discrepancy in terms of carrier type in relation to [6] can be ascribed to the higher nominal annealing temperature of 579 $^\circ$C for the $x_n = 0.15$ sample. The demonstrated ferromagnetic order in our n-type Mn-doped Bi$_2$Te$_3$ crystals has a similar ordering temperature to the p-type crystals [6]. This is in contrast to the well-known DMS Ga$_{1-x}$Mn$_x$As, in which the carrier-induced ferromagnetism is only achieved in p-type samples, and the Curie temperature has a dependence on carrier density [54, 55]. A previous study suggested a similar scenario in which the magnetic ordering in p-type Mn-doped Bi$_2$Te$_3$ should be a function of carrier density [20].

Therefore our findings are more consistent with the observation in thin film samples of Cr-doped (Bi$_{1-x}$Sb$_x$)$_2$Te$_3$ that the Curie temperature is largely independent of carrier density and type [8]. This can be seen in the carrier densities ranging between $6 \times 10^{19}$ and $3 \times 10^{20}$ cm$^{-3}$ and corresponding transport-derived $T_C$ values of 9.7 and 10.0 K, respectively. Our data agree with the suggestion of Yu et al [56] that the strong spin–orbit coupling and band inversion characteristic of the Bi$_2$(Se,Te)$_3$ family—the properties that also make them TIs—can lead to an ordered FM state largely independent of (and even without) bulk free carriers.

The results from synchrotron-radiation-based magnetometry largely confirm those obtained by the other techniques, despite being primarily surface sensitive, particularly in TEP detection method, which has a sampling depth of 3–5 nm. Furthermore, XAS and XMCD probe the charge and magnetic moment of the Mn d states, whereas the other magnetometry techniques measure the magnetic moment per volume fraction. The total magnetic moment per Mn below the Curie temperature is found to be $4.4(5) \mu_B$/Mn from magnetization measurements and $4.3(3) \mu_B$/Mn from XMCD. It is clear that below $T_C$ the Mn moments are practically 100% polarized, both in the bulk and the surface region.

The Mn XAS/XMCD spectra indicate a mixed $d^4$-$d^5$-$d^6$ ground state with a local character comparable to the DMS Ga$_{1-x}$Mn$_x$As. The 3d mixing enables ferromagnetic interactions between Mn dopants mediated by charge carriers, resulting in an interplay of magnetism and

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electrical transport. From the measured saturation moment for the bulk the valency of Mn was determined to be a mixture of 3+ and 2+. In contrast, the surface-sensitive XAS/XMCD results find a Mn valency close to 2+, as both the small positive orbital to spin moment ratio and the Anderson impurity model indicate a d-count of \( \sim 5.1 \) electrons per Mn atom. This disagrees with the theoretical predictions by Larson and Lambrecht [57] and by Zhang et al [58] who calculate a Mn valency of 3+ in Bi\(_2\)Se\(_3\) and Bi\(_2\)Te\(_3\). Further, while it is not possible to predict the precise location of the Mn dopants in the matrix of bulk crystals, it is clear from the XMCD measurements that at least some of the Mn atoms must be substitutional (on Bi sites). This can be inferred from the perpendicular magnetic anisotropy—as measured by the XMCD hysteresis curves—which can originate from the 3d spin–orbit interaction of the Mn atoms in a crystal field of the neighboring atoms. Due to the difference in valency it is therefore not possible to exclude the possibility that the region near the surface is p-doped, in contrast to the n-doped bulk.

Additionally, the magnetic transition as measured by XMCD (see figure 10(b)) is much sharper than measured by \( \mu \)SR (see figure 7(b)), indicating that the ferromagnetic order of Mn is more homogeneous in the near-surface region. Note, however, that \( \mu \)SR averages over mm-sized sample pieces, while XMC probes on a \( \mu \)-sized lateral scale (nm’s in depth) on which the sample is homogeneous judging from the very small variation of the unit cell anisotropy \((c/a)\) shown in figure 4.

The temperature-dependent Mn XMCD in a field of 6 T shows a phase transition near \( \sim 16 \) K—significantly above the \( T_C \) of \( \sim 9–13 \) K obtained from bulk-sensitive measurements, which are consistent with the values reported in the literature (e.g. [4, 6]).

Indeed, as it is clear that the surface prefers a Mn valency of 2+, and as this points toward carrier-mediated ferromagnetism, it is a possible scenario that a TI surface state with its enhanced carrier concentration could give an increased ferromagnetic transition point. However, it should be noted that this would most likely be short range magnetic order. Such a surface enhancement would provide a pathway for controlling the breaking of time reversal symmetry—potentially leading to a tunable band gap in the surface state, for example by changing doping concentration.

Our results suggest that there are different mechanisms for bulk and surface magnetism in Mn-doped Bi\(_2\)Te\(_3\), where surface magnetism could be based on a carrier-mediated process. It is hoped that future work will build on this discovery to optimize sample synthesis and thereby achieve higher transition temperatures. Unfortunately, it is clear that bulk crystals in general are simply too inhomogeneous to draw definite conclusions. A thorough multi-tool analysis conducted on a specific location on a single thin film sample, without breaking vacuum, would lead to a more consistent understanding of the materials system.

5. Conclusions

A systematic study on the structural, electric and magnetic properties of Mn-doped Bi\(_2\)Te\(_3\) single crystals has been performed. For nominal doping concentration of \( x_n = 0.09 \) the \( T_C \) is found to be between 9 and 13 K as determined by bulk-sensitive SQUID and torque magnetometry and magnetotransport measurements, and 9.4 K by \( \mu \)SR studies. XMCD measurements in a magnetic field of 6 T give a transition point of \( T \approx 16 \) K, which is ascribed to short range magnetic order.

Electron probe-based analysis finds a maximum Mn concentration in our samples of 0.11(1), indicating an apparent solubility limit, while \( \mu \)SR shows that the bulk crystals are fully
magnetized throughout their volume. Mn XAS/XMCD finds a ground state of mixed $d^4$, $d^5$ and $d^6$ character, which retains its localized electronic nature, similar to the DMS Ga$_{1-x}$Mn$_x$As. Measurements of the saturation moment with bulk-sensitive magnetization techniques give $\sim 4.4 \mu_B$/Mn, while surface sensitive XMCD gives $\sim 4.3 \mu_B$/Mn. The easy axis is along the $c$-axis, where the anisotropy constant is $\sim 11$ kJ m$^{-3}$, in agreement with Mn XMCD data showing an easy axis along the surface normal with a saturation field of $\sim 0.2$ T. The magnetic anisotropy accompanied by a small orbital magnetic moment on the Mn of 0.18 $\mu_B$ (4% of the total Mn moment), as obtained by sum-rule analysis of the Mn XMCD in saturated field at 1.8 K.

Comparison with previously reported p-type crystals [6] suggests that the magnetic ordering in Mn-doped Bi$_2$Te$_3$ is largely independent of the chemical potential of the host material. This demonstrates that the magnetic order is robust, allowing for further work to refine the electrical properties and reduce the bulk carrier density. Thin-film samples grown by molecular-beam-epitaxy may display significantly improved doping control and sample homogeneity. This will allow continuation of this work toward functionalizing TI materials into usable spintronic devices.

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