Superconductivity in Tl0.6Bi2Te3 Derived from a Topological Insulator*

Zhiwei Wang, A. A. Taskin, Tobias Frölich, Markus Braden, and Yoichi Ando

1Institute of Physics II, University of Cologne, D-50937 Cologne, Germany
2Institute of Scientific and Industrial Research, Osaka University, Osaka 567-0047, Japan

(Dated: November 7, 2018)

Bulk superconductivity has been discovered in Tl0.6Bi2Te3, which is derived from the topological insulator Bi2Te3. The superconducting volume fraction of up to 95% (determined from specific heat) with Tc of 2.28 K was observed. The carriers are p-type with the density of ~1.8 × 10^20 cm^-3. Resistive transitions under magnetic fields point to an unconventional temperature dependence of the upper critical field Bc2. The crystal structure appears to be unchanged from Bi2Te3 with a shorter c lattice parameter, which, together with the Rietveld analysis, suggests that Tl ions are incorporated but not intercalated. This material is an interesting candidate of a topological superconductor which may be realized by the strong spin-orbit coupling inherent to topological insulators.

I. INTRODUCTION

The advent of topological insulators has created an exciting interdisciplinary research field which is vitalized by discoveries of new materials to realize new concepts[1–10] and hence is greatly helped by contributions from chemistry[11]. The topological insulators are characterized by a gapped bulk state and gapless surface or edge states whose gapless nature is protected by time-reversal symmetry. Soon after the discovery of topological insulators, it was recognized that a similar topological state is conceivable for superconductors which also have a gapped bulk state[12]. Already various schemes for realizing such a topological superconductor (TSC) have been discussed[13–15] inspired by the interest in exotic quasiparticles called Majorana fermions which may show up in TSCs[16]. In particular, it has been proposed[17] that superconductors derived from topological insulators are promising candidates of TSCs due to the strong spin-orbit coupling which would lead to unconventional electronic pairing. For superconductors of this category, a limited number of materials, such as Cu_{x}Bi_{2}Se_{3}[18–20], Bi_{2}Te_{3} under high pressure[21], In_{x}Sn_{1−x}Te[22], Cu_{x}(PbSe)_{3}(Bi_{2}Se_{3})[23], Sr_{x}Bi_{2}Se_{3}[24] and Tl_{x}Te_{3}[25] have been discovered and studied.

Among such candidate TSCs, Cu_{x}Bi_{2}Se_{3} was the first to show intriguing signatures of Majorana fermions on the surface[26]. The superconductivity in this material occurs as a result of Cu intercalation into the van der Waals gap of the parent Bi_{2}Se_{3} compound. Although superconducting Cu_{x}Bi_{2}Se_{3} can be grown by a melting method[19] the superconducting volume fraction (VF) is typically very low (up to ~20%) in melt-grown samples. It was shown that an electrochemical synthesis technique[22] yields samples with much higher superconducting VF (up to ~70%) near x = 0.3[20]. However, chemical differences between superconducting and nonsuperconducting samples of Cu_{x}Bi_{2}Se_{3} are not understood. The superconductor phase is apparently unstable and it is easily lost by heat or mechanical strain, which makes it difficult to elucidate its exact crystal structure.

Very recently, it was found that bulk superconductivity can also be achieved in Bi_{2}Se_{3} by intercalation of Sr; in the resulting Sr_{x}Bi_{2}Se_{3}, the maximum transition temperature Tc of 2.9 K and the superconducting VF of up to 90% have been reported[21,25]. Also, it has been reported that all the binary topological-insulator materials having the tetradymite structure, Bi_{2}Se_{3}, Bi_{2}Te_{3}, and Sb_{2}Te_{3}, become superconductors under high pressure[21,26,28], although it is still to be elucidated how the crystallographic and electronic structures are altered before these systems show superconductivity under pressure. Another interesting candidate of TSC is Sn_{1−x}In_{x}Te. This is derived from the topological crystalline insulator SnTe by doping In to the Sn site, after which the topological surface states are still preserved[22]. However, the topological superconducting state appears to be limited to a narrow range of x and the condition for its realization is not clear at the moment[33].

To foster the research of TSCs, further discoveries of candidate materials are desirable. In this regard, making Bi_{2}Te_{3} superconducting in ambient pressure by doping would be very useful, because it allows for direct comparison to Cu_{x}Bi_{2}Se_{3} or Sr_{x}Bi_{2}Se_{3}. Like Bi_{2}Se_{3}, pristine Bi_{2}Te_{3} consists of covalently bonded quintuple layers (QLs) having the stacking sequence of Te-Bi-Te-Bi-Te, and those QLs are held together by van der Waals force[34] which is weak enough to allow for easy exfoliation. In contrast to Bi_{2}Se_{3} in which superconductivity is known to show up upon intercalation of Cu or Sr, no robust superconductivity has been reported for intercalated Bi_{2}Te_{3}, besides a preliminary report[35] of a trace superconductivity in Pd_{x}Bi_{2}Te_{3} which has not been confirmed by other groups. In this paper, we report that doping a large amount of Tl to Bi_{2}Te_{3} results in a superconductor with a transition temperature of 2.28 K. A large superconducting VF of up to 95% determined from

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II. EXPERIMENTAL METHODS

Single crystalline samples with the nominal composition of Tl\textsubscript{x}Bi\textsubscript{2}Te\textsubscript{3} with various \( x \) values were synthesized from high-purity elemental shots of Tl (99.99\%), Bi (99.9999\%) and Te (99.9999\%). We focus on samples with \( x = 0.6 \) in this paper, and results on other \( x \) values are presented in the Supporting Information. Before the synthesis, we performed surface cleaning procedures to remove the oxide layers formed in air on the raw shots of starting materials, as described in our previous paper.\textsuperscript{6} The raw materials were then mixed with the total weight of 4.0 g and sealed in an evacuated quartz tube. The sealed quartz tubes were heated up to 1123 K and kept for 48 h with intermittent shaking to ensure homogeneity of the melt. The tubes were subsequently cooled down to 823 K at a rate of 5 K/h and, then, quenched into ice-water. We also prepared a similar sample without quenching and found that quenching is essential for obtaining superconducting samples. Large shiny single crystals with the lateral dimension of up to a few centimeters can be obtained by cleaving along the \( ab \) plane. The reference Bi\textsubscript{2}Te\textsubscript{3} crystal was grown with the same method involving quenching. In addition, we also synthesized Tl\textsubscript{x}Bi\textsubscript{2–x}Te\textsubscript{3} with exactly the same method for comparison.

The crystal structure was analyzed with X-ray diffraction (XRD) using \( \theta-2\theta \) scan performed on Rigaku Ultima-IV X-ray apparatus. The Rietveld analyses of powder XRD data were performed by using FullProf software package. The actual composition was analyzed by using inductively coupled plasma atomic-emission spectroscopy (ICP-AES) as well as energy-dispersive X-ray spectroscopy (EDX). DC magnetic susceptibility was measured in a SQUID magnetometer (Quantum Design MPMS). The in-plane transport properties were measured by a standard six-probe method, recording the longitudinal resistivity \( \rho_{xx} \) and the Hall resistivity \( \rho_{yx} \) simultaneously. The single crystal samples for transport measurements were cut into a rectangular shape with a typical size of \( 2 \times 0.5 \times 0.2 \) mm\textsuperscript{3}, and electrical contacts were made by using room-temperature-cured silver paste. The specific heat \( c_p \) was measured by a relaxation-time method using the Physical Properties Measurement System from Quantum Design equipped with a \textsuperscript{3}He probe; the addenda signal was measured before mounting the sample and was duly subtracted from the measured signal. The \( c_p \) measurements were done in 0 T as well as in various magnetic fields up to 2 T applied along the \( c \) axis.

III. RESULTS AND DISCUSSIONS

We found that quenched single crystals of Tl\textsubscript{0.6}Bi\textsubscript{2}Te\textsubscript{3} are invariably superconducting at low temperature. This composition suggests that Tl atoms are intercalated in the van der Waals gap of Bi\textsubscript{2}Te\textsubscript{3}; however, as we show in the following, the crystal structure analysis suggests that intercalation is \textit{not} taking place. Figure 1(a) shows the XRD pattern of Tl\textsubscript{0.6}Bi\textsubscript{2}Te\textsubscript{3} measured on cleaved single crystals, along with similar data for pristine Bi\textsubscript{2}Te\textsubscript{3}. The sharp reflections indicate good crystalline quality of our single crystals. Only (00l) reflections can be observed with this method, and the peaks are easily indexed by considering the rhombohedral structure of Bi\textsubscript{2}Te\textsubscript{3}.
Hence, after the doping of Tl into Bi$_2$Te$_3$, the crystal structure remains essentially the same as that of the parent compound. However, in contrast to the cases of Cu or Sr-doped Bi$_2$Se$_3$, in which those dopants are intercalated into the van der Waals gap, the (00l) diffraction peaks in Tl$_{0.6}$Bi$_2$Te$_3$ shift to higher 29 angles, as one can clearly see in the inset of Figure 1(a). This means that the lattice parameter along the c-axis gets shorter after Tl doping. Quantitatively, it decreases from 30.606(4) Å in Bi$_2$Te$_3$ to 30.438(9) Å in Tl$_{0.6}$Bi$_2$Te$_3$. This observation suggests that intercalation is not taking place in Tl$_{0.6}$Bi$_2$Te$_3$. Note that the ICP-AES analysis indicates the existence of nearly stoichiometric amount of Tl in superconducting crystals, as shown in Table S1 of Supporting Information.

We also measured powder XRD patterns of Tl$_{0.6}$Bi$_2$Te$_3$ with Cu K$_α$ radiation in Bragg-Brentano geometry on powders obtained from crushed crystals, and the results are shown in Figure 1(b) along with a Rietveld refinement. (Similar XRD data for smaller Tl contents are shown in Figure S1 of the Supporting Information without refinements.) We note, however, that after the grinding, the powdered samples are no longer superconducting. This suggests that the superconductor phase of Tl$_{0.6}$Bi$_2$Te$_3$ is unstable and is fragile against mechanical strain. Furthermore, we observed that the superconducting volume fraction in Tl$_{0.6}$Bi$_2$Te$_3$ diminishes with time when the samples are left at room temperature, even though they are kept in inert atmosphere or in vacuum; this suggests that doped Tl atoms are mobile even at room temperature. In passing, we have also tried to perform single-crystal XRD analysis, but Tl$_{0.6}$Bi$_2$Te$_3$ is so soft that preparations of small single crystals required for this kind of analysis resulted in deformed samples, making it impossible to obtain data of sufficient quality for the crystal structure analysis. The degradation of crystal quality was also apparent in powdered samples.

As one can see in Figure 1(b), the diffraction data are well described by two coexisting phases, Bi$_2$Te$_3$ and TlBiTe$_2$, when taking the preferred orientation correction into account. The TlBiTe$_2$ phase possesses a volume fraction of about 35%. Attempts to refine the occupation of the Tl ions at the intercalation or other interstitial positions in the Bi$_2$Te$_3$ phase did not yield a significant occupation, in agreement with the observation that the c lattice parameter is shorter than that in pristine Bi$_2$Te$_3$. We find a significant amount of vacancies on the Bi site (about one third), which indicates a massive occupation of the Te sites by Bi or Tl ions (i.e. Bi$_{Te}$ or Tl$_{Te}$ antisite defects). Note that Bi and Tl are indistinguishable in X-ray diffraction due to their similar atomic numbers. For the Rietveld refinement, the structure of Bi$_2$Te$_3$ with symmetry R3m (lattice constants $a = b = 4.3850(16)$ Å, $c = 30.438(9)$ Å, and $γ = 120°$) with additional Tl positions was used. The position of the Bi-atoms was refined to $(0, 0, 0.39888(3))$ at the Wyckoff position 6c, the positions of the Te-atoms were $(0, 0, 0)$ at the Wyckoff position 3a and $(0, 0, 0.8043(2))$ at the Wyckoff position 6c. No significant occupation of additional Tl-atoms at $(0.5, 0.5, 0.5)$ or $(0.0, 0.0, 0.5)$ could be determined. All positions refer to the hexagonal setting of the rhombohedral cell. The TlBiTe$_2$ impurity phase was also described in space group R3m (lattice constants $a = b = 4.539(1)$ Å, $c = 22.617(8)$ Å, and $γ = 120°$) and only the z position of the Te site was refined to $(0, 0, 0.2446(10))$.

Although TlBiTe$_2$ was reported to become superconducting below 0.14 K, this impurity phase cannot be responsible for the appearance of the superconductivity in our samples, whose $T_c$ is above 2 K. It is also worth mentioning that elemental thallium metal is superconducting with $T_c$ of $\sim$2.4 K, which is close to the $T_c$ of Tl$_{0.6}$Bi$_2$Te$_3$. However, it is very unlikely that the superconductivity observed here is due to elemental thallium, because the XRD data do not indicate the existence of thallium metal in our samples.

In the past, the crystal structure of Tl-doped Bi$_2$Te$_3$ with the composition of Tl$_x$Bi$_{2-x}$Te$_3$ was studied. It was concluded that, even though the composition suggests that Tl atoms partially substitute the Bi sites of the Bi$_2$Te$_3$ lattice, what actually happens is that Tl nucleates microscopic patches of nominal Te-Bi$_{1-x}$Te$_x$-$\gamma'$ layer, which is derived from TlBiTe$_2$ structure and has the same symmetry as the Bi$_2$Te$_3$ phase (in real crystals, the fictitious plane of Te vacancy would be partially filled with Te, distributing $\gamma''$ to the neighboring Te plane of Bi$_2$Te$_3$). It was proposed that there are random microscopic formations of this defect layer Tl-doped Bi$_2$Te$_3$, which results in the overall crystal structure to be the same as Bi$_2$Te$_3$ and causes little change in the lattice constants, even though a significant amount of Tl is incorporated into the lattice.

It is useful to note that both our ICP-AES and EDX analyses of the crystals indicate the presence of nearly stoichiometric amount of Tl, which would give rise to about 30% of the TlBiTe$_2$ phase if the sample phase-separates into Bi$_2$Te$_3$ and TlBiTe$_2$. The amount of the TlBiTe$_2$ phase indicated in the Rietveld refinement is consistent with this estimate, which suggests that due to the mobility of Tl atoms at room temperature, the material actually phase separates into Bi$_2$Te$_3$ and TlBiTe$_2$ upon grinding. This in turn suggests that it is very difficult to elucidate the crystal structure of the superconductor phase.

A possible picture, which one can speculate for the superconducting phase based on the above result, would be to consider the formation of the nominal Te-Bi$_{1-x}$Te$_x$-$\gamma'$ defect layer in the Bi$_2$Te$_3$ lattice, as is the case of the Tl$_x$Bi$_{2-x}$Te$_3$ compound. This defect layer may eventually cluster to form the TlBiTe$_2$ phase. An important difference from the case of the Tl$_x$Bi$_{2-x}$Te$_3$ compound would be that a sizable portion of Bi atoms in Tl$_{0.6}$Bi$_2$Te$_3$ are most likely partially filling the Te sites of the Bi$_2$Te$_3$ lattice and form Bi$_{Te}$ antisite defects, which is consistent with the result of the Rietveld refinement. In fact, the composition of Tl$_{0.6}$Bi$_2$Te$_3$ would create a sig-
nificantly Te-deficient growth condition and promote the formation of Bi$_2$Te$_3$ antisite defects.\textsuperscript{11} In any case, the precise structure of superconducting Tl$_{0.6}$Bi$_2$Te$_3$ should be determined in future studies, possibly by neutron scattering on as-grown crystals.

Figure 2 shows the temperature dependence of $\rho_{xx}$ in Tl$_{0.6}$Bi$_2$Te$_3$ at zero field. The onset of superconducting transition occurs at $T \approx 2.42$ K, and the zero resistivity is achieved at $T \approx 2.15$ K (lower inset of Figure 2), indicating a relatively sharp transition. The resistivity in the normal state shows a metallic behavior with the residual resistivity $\rho_0 = 2 \times 10^{-4}$ $\Omega$cm. The magnetic-field dependence of $\rho_{xx}$ at 2.5 K is shown in the upper inset of Figure 2; this $\rho_{xx}(B)$ behavior is slightly non-linear, which suggests the existence of two or more bands at the Fermi level. Also, the $\rho_{xx}(B)$ data indicate that the main carriers are $p$-type (i.e., holes), and from the slope near 0 T we calculate the approximate carrier density of $p \approx 1.8 \times 10^{20}$ cm$^{-3}$. From $\rho$ and $\rho_0$, one obtains the mobility $\mu \approx 175$ cm$^2$/Vs. It is important to note that the carrier type is different from the case of Cu$_2$- or Sb-intercalated Bi$_2$Se$_3$ superconductors, in which the carriers are $n$-type.\textsuperscript{19,20} Nevertheless, the magnitude of the carrier density, about $2 \times 10^{20}$ cm$^{-3}$, is comparable to that in Cu$_2$Bi$_2$Se$_3$.\textsuperscript{19,20} Hence, Tl$_{0.6}$Bi$_2$Te$_3$ would allow for investigation of the roles of the carrier types in producing a topological superconducting state in otherwise similar settings, if this material turns out to be a TSC.

In passing, we comment on the possible impact of the TIBi$_2$Te$_3$ impurity phase and the nominal Te-Bi$_2$Te-$V_{Te}^{\bullet \bullet}$ defect layer on the transport properties. While the direct impact of phase-separated TIBi$_2$Te$_3$ impurity phase is expected to be minor because the carrier density of this phase is similar to that of the main phase,\textsuperscript{27} the defect layer may be working as strong scatterers of charge carriers and is possibly playing some role in the occurrence of superconductivity.

Figure 3(a) shows the temperature dependence of the shielding fraction in Tl$_{0.6}$Bi$_2$Te$_3$ measured under 0.2 mT applied parallel to the $ab$-plane to minimize the demagnetization effect; the configuration is schematically shown in the inset. Note that the shielding fraction is defined as the fraction of the sample volume from which the magnetic field is kept out due to superconductivity; the data for both field-cooled (FC) and zero-field-cooled (ZFC) measurements are shown. The onset of superconducting transition is observed at $T \approx 2.35$ K. This is consistent with the resistivity transition shown in Figure 2. Furthermore, the ZFC shielding fraction at 1.75 K is as much as 83%, pointing to bulk superconductivity.

We have also synthesized Tl$_{x}$Bi$_2$Te$_3$ samples with various $x$ values, and it was found that both $T_c$ and the shielding fraction become lower for $x < 0.6$, as is shown in Figure S2 of the Supporting Information. Also, for $x > 0.6$, we found that the TIBi$_2$Te$_3$ impurity phase becomes dominant and it was impossible to synthesize large single crystals retaining the Bi$_2$Te$_3$ structure. Therefore, we concluded that $x = 0.6$ is the optimum composition for this new superconductor.

The magnetization curve $M(B)$ measured at 1.75 K with the magnetic field applied parallel to the $ab$ plane is shown in Figure 3(b). This $M(B)$ behavior indicates that Tl$_{0.6}$Bi$_2$Te$_3$ is a type-II superconductor and the flux pinning is very weak, as was also the case in Cu$_2$Bi$_2$Se$_3$.\textsuperscript{20} From the low-field $M(B)$ behavior measured after zero-field cooling (shown in Figure S3 of Supporting Information), one can determine the lower critical field $B_{c1}$ as the characteristic field above which the $M(B)$ data start to deviates from the initial linear behavior; at the lowest temperature of 1.75 K, $B_{c1}$ is estimated to be 0.35 mT, which is very small and is comparable to that in Cu$_2$Bi$_2$Se$_3$.\textsuperscript{19,20} Such a low $B_{c1}$ value means a very low superfluid density, which is consistent with the low carrier density.

Figure 4 shows the plots of $c_p/T$ vs $T$ measured in 0 T and 2 T applied perpendicular to the $ab$-plane, as schematically shown in the inset; since the superconductivity is completely suppressed in 2 T as we show later, the 2-T data represent the normal-state behavior. A fit of the normal-state data to the conventional Debye formula $c_p = \gamma_n T + A_3 T^3 + A_5 T^5$, shown as the dashed line in Figure 4(a), gives the following parameters: $\gamma_n = 4.8$ mJ/mol-K$^2$, $A_3 = 4.4$ mJ/mol-K$^4$, and $A_5 = 0.11$ mJ/mol-K$^6$. The electronic specific heat $c_{el}/T$ in the SC state is obtained by subtracting the phononic contribution $A_3 T^3 + A_5 T^5$ from the zero-field data, and the result is plotted in Figure 4(b). The pronounced jump gives evidence for the bulk nature of the superconductivity in Tl$_{0.6}$Bi$_2$Te$_3$, and this anomaly provides an accurate measure of $T_c = 2.28$ K. Fitting of $c_{el}(T)/T$ to the BCS model\textsuperscript{42} reproduces the zero-field data very well if one assumes a 95% superconducting VF. Therefore, one may conclude that the superconducting state of Tl$_{0.6}$Bi$_2$Te$_3$ is fully gapped. Note that the applicability of the BCS model to the specific-heat data does not exclude the possibility of unconventional odd-parity.
The superconducting VF of 95% is incompatible with the 35% inclusion of TIBiTe2 phase suggested by the Rietveld analysis on crushed crystals, and this incompatibility supports our speculation that a sizable amount of TIBiTe2 phase is created upon grinding.

To determine the upper critical field $B_{c2}$, the magnetic-field dependences of $\rho_{xx}$ at various temperatures down to 0.42 K were measured in fields perpendicular to the $ab$-plane [Figure 5(a)]. For the analysis of the resistive transitions, both the 50% and 90% levels of the normal-state resistivity $\rho_N$ (shown by dashed lines) are taken as characteristic levels to mark the transition; the difference between these two criteria gives an idea about the uncertainly in determining $B_{c2}$ from resistive transitions. In addition, the $c_{el}(T)/T$ behavior was measured in various magnetic-field strengths [Figure 5(b)], and we take the mid-point of the specific-heat jump as the definition of the thermodynamic transition. Note that the data shown in Figures 2 – 5 are all taken on the same sample. The summary of $B_{c2}$ thus determined are plotted in Figure 5(c). The Werthamer-Helfand-Hohenberg (WHH) theory\(^\text{13}\) fits the thermodynamic $B_{c2}(T)$ obtained from specific heat very well and gives $B_{c2}(0)$ of 1.06 T, which corresponds to the coherence length $\xi = \sqrt{\Phi_0/(2\pi B_{c2})} = 17.6$ nm. On the other hand, the $B_{c2}(T)$ extracted from resistive transitions do not follow the WHH behavior and extrapolates to a higher $B_{c2}(0)$; such a behavior has been reported for Cu$_x$Bi$_2$Se$_3$ and also for pressurized Bi$_2$Se$_3$, and was argued as evidence for unconventional superconductivity\(^\text{24,44}\).

IV. CONCLUSIONS

The discovery of superconductivity in Tl$_{0.6}$Bi$_2$Te$_3$ widens the opportunities to elucidate topological superconductivity in topological-insulator-based superconductors, particularly since the superconducting VF of up to 95% is achievable. Various aspects of the superconductivity in Tl$_{0.6}$Bi$_2$Te$_3$, including the unconventional resistive $B_{c2}(T)$ behavior and the very small $B_{c1}$ value, are similar to those found in Cu$_x$Bi$_2$Se$_3$. Nevertheless, the carrier type is opposite, which may prove useful for understanding the mechanism of superconductivity. The crystal structure of this material appears to be essentially unchanged from that of Bi$_2$Te$_3$ with a slightly shorter $c$-axis length and no interstitials, but it turned out to be difficult to elucidate the exact structure of the superconductor phase.

V. SUPPORTING INFORMATION

Table showing the results of ICP-AES analysis; powder XRD data for smaller Tl contents; superconducting transitions in crystals with smaller Tl contents probed...
by magnetic susceptibility; virgin $M(B)$ curve for determining $B_{c1}$.

and the Excellence Initiative of the German Research Foundation.

VI. ACKNOWLEDGMENT

This work was supported by Japan Society for the Promotion of Science (KAKENHI 25220708 and 25400328)

† Electronic address: ando@ph2.uni-koeln.de

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Supporting Information

| $x$ | Nominal composition | Tl   | Bi   | Te  |
|-----|---------------------|------|------|-----|
| 0.1 | Tl$_{0.1}$Bi$_2$Te$_3$ | 0.106(1) | 2.087(6) | 3   |
| 0.2 | Tl$_{0.2}$Bi$_2$Te$_3$ | 0.207(2) | 2.098(6) | 3   |
| 0.3 | Tl$_{0.3}$Bi$_2$Te$_3$ | 0.233(2) | 2.090(6) | 3   |
| 0.4 | Tl$_{0.4}$Bi$_2$Te$_3$ | 0.396(4) | 2.077(6) | 3   |
| 0.5 | Tl$_{0.5}$Bi$_2$Te$_3$ | 0.526(5) | 2.040(6) | 3   |
| 0.6 | Tl$_{0.6}$Bi$_2$Te$_3$ | 0.609(6) | 2.059(6) | 3   |

**TABLE I:** Molar ratio of Tl, Bi, and Te in the single-crystal samples of Tl$_x$Bi$_2$Te$_3$. The data are obtained from ICP-AES analyses. The tellurium composition is fixed to be 3.

![XRD patterns](image)

**FIG. S1:** Powder XRD patterns of Tl$_x$Bi$_2$Te$_3$ ($x = 0.1, 0.2, 0.3, 0.4,$ and $0.5$) and Bi$_2$Te$_3$, taken on powders prepared by crushing cleaved single crystals. The peaks due to the TlBiTe$_2$ impurity phase are indicated with asterisks, and they are discernible in the data for $x = 0.3, 0.4,$ and $0.5$. 
FIG. S2: Temperature dependence of the magnetic susceptibility in Tl$_x$Bi$_2$Te$_3$ with $x = 0.1 - 0.5$ measured under 0.2 mT, plotted in terms of the shielding fraction.

FIG. S3: Virgin $M(B)$ curve of Tl$_{0.6}$Bi$_2$Te$_3$ at 1.75 K measured after zero-field cooling the sample. The magnetic field was applied parallel to the $ab$ plane to minimize the demagnetization effect.