Syntheses, Crystal Structure and Magnetic Properties of Tl$_9$RETe$_6$ (RE = Ce, Sm, Gd)

Anna Isaeva $^{1,2}$, Rico Schönemann $^{3,*}$ and Thomas Doert $^{4,*}$

$^1$ Faculty of Physics, Technische Universität Dresden, D–01062 Dresden, Germany; anna.isaeva@tu-dresden.de
$^2$ Leibniz Institute for Solid State Research, IFW Dresden, D–01069 Dresden, Germany
$^3$ Hochfeld-Magnetlabor (HLD-EMFL), Helmholtz-Zentrum Dresden Rossendorf, D–01328 Dresden, Germany; r schoenemann@lanl.gov
$^4$ Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, D–01062 Dresden, Germany
* Correspondence: thomas.doert@tu-dresden.de; Tel.: +49-351-463-33864
† Present address: MPA-MAGLAB, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

Received: 17 March 2020; Accepted: 2 April 2020; Published: 7 April 2020

Abstract: The three compounds Tl$_9$RETe$_6$ with RE = Ce, Sm, Gd were synthesized from the elements at 1020 K. Their isostructural crystal structures are ordered derivatives of the Tl$_5$Te$_3$ type with rare-earth metal and thallium occupying different Wyckoff positions. The structures can be understood as charge-ordered in accordance with the Zintl-Klemm concept: 9 Tl$^+$ + RE$^{3+}$ + 6 Te$^{2-}$. DFT calculations for Tl$_9$GdTe$_6$, however, result in a low, but finite density of states at the Fermi level. Magnetic data confirm trivalent Gd, but indicate a small amount of Ce$^{4+}$ in Tl$_9$CeTe$_6$; no indications for long-range magnetic order was found down to $T = 2$ K.

Keywords: Tellurides; thallium; rare-earth metals; crystal structure; magnetic properties

1. Introduction

Tl$_5$Te$_3$ and its derivatives have attracted considerable attention as thermoelectric materials [1–11] and recently as topological materials with a superconducting phase below 2.4 K [12]. Binary Tl$_5$Te$_3$ is known to adopt the In$_5$Bi$_3$ type structure (space group I4/mcm, $a = 893.0(2)$ pm, $c = 1258.9(4)$ pm), with two distinct Tl positions (T11 on Wyckoff site 4c and TII on 16i) and two Te positions (Te1 on 4a, Te2 on 8i) [12,13]. Several ternary derivatives of the types Tl$_9$MTe$_6$ (M = Sb, Bi), Tl$_9$RETe$_6$ (RE = rare earth metal) and Tl$_9$M Te$_5$ (M’ = Cu, Sn, Pb, Mo) have been reported [1–11,14–21]. Substitutions have generally been found to occur on Wyckoff site 4c preferably. The composition Tl$_9$M’Te$_3$ could in principle be realized by complete substitution of TlII on Wyckoff site 4c, the composition Tl$_9$MTe$_6$ corresponds to a substitution of one-half of the TlII atoms. Mixed M/Tl occupancies on the 4c site were reported for Tl$_{10-x}$RE$_x$Te$_6$ (RE = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er, with $0 < x < 1.32$), e.g., [6,9]. Magnetization data for the compounds Tl$_{10-x}$RE$_x$Te$_6$, RE = Ce, Pr, Tb, Sm point at paramagnetic behavior in low fields down to $T = 2$ K and the extracted effective paramagnetic moments indicate (with the exception of Ce) trivalent rare earth metals [10]. Therefore, a charge ordered formula for the composition Tl$_9$RETe$_6$ could be written as 9 Tl$^+$ + RE$^{3+}$ + 6 Te$^{2-}$ in accordance with the semiconducting properties of these compounds [9]. Moreover, it may as well give rise to the formation of a two-fold superstructure with full ordering of M$^{3+}$ and Tl$^+$ atoms.

The progenitor of the series Tl$_5$Te$_3$ has a non-trivial topology of the electronic band structure due to a band inversion between the TII and Te states of opposite parity at the Z point of the 3D Brillouin zone [12]. Given the current interest in quantum materials that combine non-trivial topology and intrinsic magnetic order [22], we re-investigated the crystal structures and magnetic properties of Tl$_9$RETe$_6$ with RE = Ce, Sm, Gd on single crystals. Such compound in a magnetically ordered state...
would be a candidate magnetic topological semimetal. We aim to provide the crystallographic data of highest possible quality and precision for the first-principles calculations, since topological properties depend on the fine details of lattice symmetries. The results are presented in the following.

2. Materials and Methods

2.1. Synthesis

All preparation steps were carried out in an argon (99.996% Messer-Griesheim, Sulzbach, Germany) filled glovebox (MBraun, Garching, Germany). The title compounds were obtained by direct synthesis of the elements in stoichiometric amounts, typically aiming at a sample mass of 1.5 g per batch. The rare-earth metals (Ce, Gd, Sm: 99.9%, Strem, Kehl, Germany) were rasped from compact blocks and Tl (99.9% Alfa Aesar, Karlsruhe, Germany) was cut from a rod. The metal pieces were filled in silica ampoules with glassy carbon crucibles together with the calculated amount of Te (lump 99.999%, Alfa Aesar, Karlsruhe, Germany). The ampoules were flame sealed and placed in a furnace, heated to 1020 K for 24 h and cooled to ambient temperature with 5 K/h.

The resulting ingots are dark-grey with metallic luster. The materials are brittle and can easily be crushed. Some parts were further ground for powder X-ray and magnetic measurements. Crystals for structure determination could be selected from the crushed ingots.

2.2. X-ray Powder Diffraction

X-ray powder diagrams (powder diffractometer XPert Pro, PANalytical GmbH, Kassel, Germany; CuKα radiation, Bragg-Brentano setup) were recorded to check for phase purity and to determine the lattice parameters. Moreover, Rietveld fits were performed to refine the lattice parameters and to check the structure model derived from single crystal data for consistency [23].

2.3. Energy Dispersive X-ray Spectroscopy (EDX)

Energy dispersive X-ray (EDX) analyses were performed in a SEM SU 8020 (Hitachi High-Technologies Europe GmbH, Krefeld, Germany) equipped with a silicon drift EDX detector XMAXN (Oxford Instruments, Wiesbaden, Germany) at 30 kV acceleration voltage. Crystals of the phase pure samples were embedded in a conductive polymer matrix, cut and polished to provide a plane and clean surface. Analyses were made by averaging on several points and line scans of different crystals for each sample according to the fundamental parameter method applying a PAP matrix correction [24].

2.4. Crystal Structure Determination

Single crystal experiments were performed on a Kappa Apex II CCD diffractometer (Bruker-AXS GmbH, Karlsruhe, Germany) with Mo Kα radiation using the software package Apex Suite [25]. A multi-scan absorption correction was employed [26]. Atom parameters and atom designations for structure refinement with JANA 2006 [23] were derived by the symmetry reduction stated in the Discussion, see below. Diamond 4 was used for structure visualization [27].

2.5. Electronic Structure Calculations

Density functional theory (DFT) calculations within the local density approximation with Hubbard correction (LDA+U) using the around mean field (AFM) double counting were performed for Tl9GdTe6 in the full-potential full-electron linear augmented plane-wave (FP-LAPW) code [28]. Spin-orbit coupling was taken into account fully-relativistically. The values of Hubbard U = 6.7 eV and J = 0.7 eV were chosen to treat the Gd d-orbitals. These optimized parameters were reported for the electronic structure of pure gadolinium metal and we tested them to reproduce the magnetic moments on Gd atoms with our program code [29]. Formal charges were calculated according to the Bader partitioning scheme [30].
2.6. Magnetic Measurements

Magnetization measurements on samples of Tl$_9$CeTe$_6$ and Tl$_9$GdTe$_6$ were carried out with a commercial superconducting quantum interference device (SQUID) magnetometer MPMS (Quantum Design Europe, Darmstadt, Germany) in a temperature range of 300 K $\leq T \leq$ 2 K.

3. Results and Discussion

EDX analyses performed on several of the as-grown crystals of each sample confirm the composition of the compounds within the limit of the method, although a slight excess of Te was observed for all samples, Table 1. No hints for contaminations or defects were obtained.

Table 1. Energy dispersive X-ray (EDX) derived composition of Tl$_9$RETe$_6$ (atom-%), stated are average values from different crystals of each sample.

| Element | Tl$_9$CeTe$_6$ | Tl$_9$SmTe$_6$ | Tl$_9$GdTe$_6$ | Theor. |
|---------|----------------|----------------|----------------|-------|
| RE      | 5.7(4)         | 5.9(4)         | 6.4(2)         | 6.2   |
| Tl      | 56.0(3)        | 55.3(5)        | 55.1(3)        | 56.3  |
| Te      | 38.3(3)        | 38.8(2)        | 38.5(4)        | 37.5  |

According to the X-ray powder patterns and the respective Rietveld fits, phase-pure samples of Tl$_9$CeTe$_6$, Tl$_9$SmTe$_6$ and Tl$_9$GdTe$_6$ were obtained, cf. Figure 1 as an example and also Figure S1. The tetragonal lattice parameters derived from powder X-ray data are in good agreement with those from single crystal experiments (Table 2).

Figure 1. Experimental X-ray powder data (black) and Rietveld fit (blue line) for Tl$_9$GdTe$_6$ as example; the positions of the Bragg reflections and the difference plot are shown in the lower part; CuK$_\alpha$, $\lambda$ = 1.54051 Å. Profile R factors: GOF = 1.84, $R_p$ = 3.81 w$R_p$ = 6.08.

Analyses of the single-crystal data sets of the compounds Tl$_9$CeTe$_6$, Tl$_9$SmTe$_6$ and Tl$_9$GdTe$_6$ indicated body-centered tetragonal unit cells each. For all three compounds, a considerable number of reflections with intensities well above a threshold of 3$sigma(I)$ were found to contradict glide planes and screw axes. Moreover, depending on the twin volume ratio (cf. below), the $R_{int}$ value for symmetry averaging was found to be significantly lower for Laue class 4/m as compared to Laue class 4/mmm.
(e.g., 0.071 vs. 0.125, respectively, for Tl9SmTe6). These findings refute space group I4/mcm and point towards I4/m instead.

Structure solutions were hence made in I4/m and refinements proceeded smoothly to the results and residuals stated in Table 2. Space group I4/m provides a possibility for Tl⁺ and RE³⁺ ions to reside on two crystallographically independent sites, as has been described for SbTl9Te6 in a similar way [20]. The symmetry and structure relations between Tl3Te3 in space group I4/mcm and those of the title compounds Tl9RETe6 (RE = Ce, Sm, Gd) is depicted in the Bärnighausen diagram in Figure 2. The occupancies of the Tl1 (Wyckoff site 2a) and the RE atoms (2b) were found to be unity within an uncertainty interval of 3σ in the refinements. No experimental evidence for a mixed occupancy on the 2a and 2b sites was found, as for any other Wyckoff site. The main crystallographic data and refinement details are stated in Tables 2 and 3, selected interatomic distances are listed in Table 4. Crystallographic data have been deposited with the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) and can be obtained on quoting the depository number CSD-427736 (Tl9CeTe6), CSD-427737 (Tl9GdTe6) and CSD-427738 (Tl9SmTe6). Note, that despite the evidence of the reflection conditions refuting the higher symmetric space group I4/mcm, refinements in this space group were performed for reasons of comparison with previously published data. These refinements, as can be seen from Table S1, Supporting Information, resulted in unsatisfactory R-values and much higher difference Fourier peaks in all three cases and underline the correct choice of space group I4/m additionally.

Table 2. Crystallographic data and refinement parameters of Tl9RETe6.

| Chemical Composition | Tl9CeTe6 | Tl9SmTe6 | Tl9GdTe6 |
|----------------------|----------|----------|----------|
| $M_r$/g mol⁻¹, F(000) | 2745.1, 2189 | 2755.4, 2206 | 2762.3, 2210 |
| temperature/K | 295(1) | | |
| diffractometer type | Kappa Apex II CCD (Bruker-AXS) | | |
| wavelength/Å | 0.71069 (Mo Kα, graphite monochromator) | | |
| crystal system | tetragonal | | |
| space group (No.), Z | I4/m (no. 87), 2 | | |
| cell parameters *, a/pm | 890.48(2) | 886.50(5) | 887.00(3) |
| c/pm | 1313.42(5) | 1306.41(6) | 1306.56(5) |
| cell volume/10⁶ pm³ | 1041.48(5) | 1026.7(1) | 1027.96(6) |
| density/g cm⁻³ | 8.75 | 8.91 | 8.92 |
| Abs. coefficient/mm⁻¹ | 79.69 | 81.48 | 81.75 |
| absorption correction | multi-scan (SADABS [26]) | | |
| crystal size / mm³ | 0.289/0.749 | 0.292/0.746 | 0.499/0.747 |
| measurement range | 0.189 × 0.057 × 0.045 | 0.021 × 0.027 × 0.043 | 0.075 × 0.061 × 0.035 |
| | 2.8 ≤ θ ≤ 42.6 | 2.8 ≤ θ ≤ 34.7 | 2.8 ≤ θ ≤ 35.2 |
| | −13 ≤ h ≤ 15 | −11 ≤ h ≤ 14 | −14 ≤ h ≤ 13 |
| | −15 ≤ k ≤ 15 | −9 ≤ k ≤ 14 | −14 ≤ k ≤ 11 |
| | −15 ≤ l ≤ 24 | −20 ≤ l ≤ 20 | −17 ≤ l ≤ 19 |
| $R_{int}$ | 0.0328 | 0.071 | 0.030 |
| refinement | JANA2006, full-matrix least squares on $F^2$ [23] | | |
| reflections, with I > 3σ(I), parameters | 1693, 1458, 25 | 1153, 795, 24 | 1151, 830, 25 |
| extinction parameter | 0.118(2) | - | 0.0059(7) |
| goodness-of-fit | 1.5 | 1.1 | 1.2 |
| $R_1$(obs), wR2(obs) | 0.031, 0.065 | 0.035, 0.062 | 0.026, 0.049 |
| $R_1$(all), wR2(all) | 0.038, 0.066 | 0.059, 0.069 | 0.050, 0.055 |
| twin matrix | 0 1 0, 1 0 0, 0 0 −1 | | |
| twin volume fraction | 0.518(2) | 0.672(2) | 0.997(1) |
| $\Delta p_{\min}$ / $\Delta p_{\max}$, e/10⁶ pm³ | 2.57/−2.02 | 2.02/−3.38 | 2.29/−2.12 |

* from powder data
The average Sm–Te distances in the octahedra is 312.6(1) pm and thus about 10% shorter than the average Tl1–Te distance of 345.1(1) pm for the Tl1Te6 octahedra. For comparison: the Tl1Te6 octahedron in the Tl9SmTe6 title compounds.

As the three title compounds Tl9CeTe6, Tl9SmTe6 and Tl9GdTe6 are isotypic, the structure description and discussion are exemplified by Tl9SmTe6. The structures of Tl5Te3 and some of its derivatives have been discussed in several publications; however, authors have emphasized different structural details. Focus was laid on the stacking of two different sets of interpenetrating nets [14], equidistant linear Tl1–Te1 chains running along [001] [14], coordination polyhedra around Tl1 and Tl2 [15–21] or a perovskite-like arrangement of Tl1Te6-octahedra in which the large voids are occupied by Tl4-tetrahedra [12]. Figure 3 shows projections of the unit cells of Tl9SmTe6 and Tl5Te3 next to each other for comparison. As can be seen, the major difference is in the decoration of the metal sites (Tl1 and RE), other structural differences are hardly noticeable from this image.

**Table 3. Fractional coordinates and isotropic displacement parameters of Tl9RETe6.**

| Atom       | x   | y   | z   | Ueq, pm² |
|------------|-----|-----|-----|----------|
| Tl9CeTe6   |     |     |     |          |
| Ce         | 0   | 0   | 0   | 170(1)   |
| Tl1        | 0   | 0   | ½   | 252(1)   |
| Tl2        | 0.1557(1) | 0.6377(1) | 0.1600(1) | 335(1)    |
| Te1        | 0   | 0   | 0.2403(1) | 120(1)    |
| Te2        | 0.3284(1) | 0.8466(1) | 0   | 180(1)    |
| Tl9SmTe6   |     |     |     |          |
| Sm         | 0   | 0   | 0   | 173(3)   |
| Tl1        | 0   | 0   | ½   | 227(3)   |
| Tl2        | 0.1539(1) | 0.6392(1) | 0.1602(1) | 339(1)    |
| Te1        | 0   | 0   | 0.2372(1) | 201(3)    |
| Te2        | 0.3245(1) | 0.8487(1) | 0   | 185(2)    |
| Tl9GdTe6   |     |     |     |          |
| Gd         | 0   | 0   | 0   | 173(3)   |
| Tl1        | 0   | 0   | ½   | 273(3)   |
| Tl2        | 0.1539(1) | 0.6392(1) | 0.1602(1) | 339(1)    |
| Te1        | 0   | 0   | 0.2372(1) | 201(3)    |
| Te2        | 0.3245(1) | 0.8487(1) | 0   | 185(2)    |

Ueq is defined as 1/3 of the orthogonalized $U_{ij}$ tensor.

A more detailed view on the structures, especially on the Tl1Te6 and SmTe6 octahedra, however, reveals further differences. The Tl1Te6 octahedra are defined by two apical Tl–Te distances of 343.3(1) pm and four basal ones of 346.0(1) pm. The Sm atom does also reside in a slightly compressed octahedron with two apical Sm–Te distances of 302.9(1) pm and four basal ones of 317.5(1) pm. The average Sm–Te distances in the octahedra is 312.6(1) pm and thus about 10% shorter than the
average Tl1–Te distance of 345.1(1) pm for the Tl1Te6 octahedra. For comparison: the Tl1Te6 octahedron in the binary phase Tl5Te3 consists of two apical Tl–Te distances of 314.7 pm and four basal ones of 336.1 pm, resulting in an average value of 329.0 pm; for the Tl9RETe6 compounds, the average distances in the RE–Te and Tl1–Te octahedra are 320.4(1) pm and 343.3(1) pm for Tl9CeTe6 314.4(1) pm and 345.9(1) pm for Tl9GdTe6, respectively. Figure 4 illustrates the size difference by enfolding the octahedra with a sphere of the radius of the average Sm–Te and Tl1–Te distances. This spherical representation clearly evidences why the ternary compounds preferably adopt the lower symmetric structure in I4/m. In this context, the term “charge-ordered structure” does not reflect the whole truth as size-order is at least a comparable driving force.

Looking for next nearest neighbors of the Sm and Tl1 atoms, eight Tl2 atoms forming a cuboid have to be considered. The distances to the central Sm and Tl1 atoms are 409.2(1) pm and 391.3(1) pm, respectively. The Te1 atoms are surrounded by a square antiprism of eight Tl2 atoms with both square faces capped by Tl1 or Sm atoms, Figure 5.

Figure 3. View on the unit cells of Tl9SmTe6 (left) and Tl5Te3 (right, [14]).

Figure 4. Size difference of the SmTe6 (green) and Tl1Te6 (dark grey) octahedra; the radius of a sphere is the average distance to the coordinating Te atoms.
Tl₅Te₃, Tl₅Se₃ and their ternary derivatives can, at least formally, be written on the basis of a Zintl-like charge-ordered formula in the first approach. For the rare-earth metal substituted compounds Tl₀RETe₆, this would result in 9 Tl⁺ + RE³⁺ + 6 Te²⁻. The sizes of the metal coordination octahedra can then be rationalized according to the ionic radii of the respective Tl⁺ and RE³⁺ metal ions: 164 pm for Tl⁺, 115 pm for Ce³⁺, 110 pm for Sm³⁺ and 108 pm for Gd³⁺, all for octahedral coordination [31]. The smaller TlTe₆ coordination polyhedron in Tl₅Te₃ as compared to those in Tl₀RETe₆ is also understandable: In Tl₅Te₃ one fifth of the Ti atoms (i.e., the Ti atoms on 4c in space group I₄/mcm) can be considered to be in an intermediate 2+ valence state: 4 Tl⁺ + Ti²⁺ + 3 Te²⁻ [32]. However, the formulation as mixed-valent compound according to 9 Tl⁺ + Ti³⁺ + 6 Te²⁻ is conceivable, yet not supported by crystallographic evidence.

**Table 4. Selected interatomic distances (pm) of Tl₀RETe₆.**

| Compound | Metal | Te | 2× | Ti | 2× |
|----------|-------|----|----|----|----|
| Tl₅CeTe₆ | Ce-   | Te1 | 315.7(1) | Tl1- | Te1 | 341.1(1) |
|          | Te2   | 322.8(1) | Tl2- | Te2 | 344.4(1) |
|          | Tl2   | 409.2(1) | Tl2- | Tl2 | 391.4(1) |
| Tl₅SmTe₆ | Sm-   | Te1 | 309.9(1) | Tl1- | Te1 | 343.3(1) |
|          | Te2   | 317.5(1) | Tl2- | Te2 | 346.0(1) |
|          | Tl2   | 405.9(1) | Tl2- | Tl2 | 391.3(1) |
| Tl₅GdTe₆ | Gd-   | Te1 | 309.4(1) | Tl1- | Te1 | 343.9(1) |
|          | Te2   | 316.9(1) | Tl2- | Te2 | 346.9(1) |
|          | Tl2   | 405.7(1) | Tl2- | Tl2 | 392.0(1) |

**Figure 5.** Extended coordination polyhedra for Sm (left) and Ti1 atoms (right): slightly compressed Te₆ octahedra plus Tl₈ cuboid.
Based on the crystallographic data, we perform preliminary spin-polarized band-structure calculations for Tl₉GdTe₆ and find that a ferromagnetically ordered state is more energetically favorable than a non-magnetic configuration. Figure 6 shows the full-relativistic bulk electronic spectrum, which is metallic with low yet finite electron density at the Fermi energy. This is in line with the experimentally observed electronic conductivity [8]. At about 0.2 eV below the Fermi level the electron density drops to almost zero and there is an (avoided) band crossing at the Γ point. This feature is constituted by Tl and Te states, while the majority of Gd f-states reside at ca. −10 eV. These spin-polarized bands may either hybridize and open a tiny gap or form a protected crossing. In both cases, Tl₉GdTe₆ could be a candidate topological material: either a topological insulator or a topological semimetal. These scenarios call for further in-depth elucidation. The calculated effective magnetic moment amounts to 7.4 µB/Gd atom. This value is slightly lower than the theoretical moment of 7.98 µB for Gd³⁺ [33], the discrepancy likely pointing towards a certain degree of electron delocalization in a metallic system. The computed formal charges are: Tl₁: +0.3, Tl₂: +0.3, Gd: +0.55, Te₁: −0.5, Te₂: −0.5.

Magnetic measurements performed on samples of Tl₉CeTe₆ (Figure S2) and Tl₉GdTe₆ (Figure 7) demonstrate that both compounds are paramagnetic in the temperature interval 2 K < T < 300 K and no long-range magnetic order was established. The Curie–Weiss fit for Tl₉CeTe₆ results in a magnetic moment of 2.18 µB per Ce-atom, in accordance with [10]. The values are slightly reduced with respect to the expected value of 2.51 µB for a pure Ce³⁺ (J = 5/2) system [33] and might point towards a small amount of Ce⁴⁺. For Tl₉GdTe₆, the Curie–Weiss fit yields 8.12 µB per Gd atom for the Gd compound in reasonable agreement with the expected value for a J = 7/2 system of 7.98 µB [33]. Whereas binary Tl₅Te₃ turns superconducting at Tc = 2.4 K [12], we find no indication for superconductivity for the Ce- and Gd-substituted samples. The RE substitution seems at least to lower the T_c noticeably.
4. Conclusions

In contrast to previous investigations, the stoichiometrically substituted tellurides Tl9CeTe6, Tl9SmTe6 and Tl9GdTe6 were found to adopt an ordered variant of the In5Bi3 type, which allows for an adaption of the different metal atom sizes. The compounds crystallize in space group 14/m (no. 87) and the structures can be understood as charge-ordered in accordance with a Zintl-type formula (Tl+)9(RE3+)(Te2−)6. Spin-polarized DFT calculations for Tl9GdTe6 result in a low, but finite density of states at the Fermi level. The experimental transport behavior determined on hot-pressed powder samples points towards $p$-type semiconductors for the Tl9RETe6 compounds with relatively high conductivity values at ambient temperature. Our preliminary calculations also indicate a possibility for non-trivial topology of the electronic structure, which will be studied in full detail elsewhere. There is an (avoided) band crossing at the $\Gamma$ point of the 3D Brillouin zone at ca. 0.2 eV below the Fermi level. Thus, Tl9GdTe6 may become a candidate topological material upon $p$-doping and given a ferromagnetic ordering. The calculated ground state is ferromagnetic with 7.4 $\mu_B$/Gd-atom, however, magnetization measurements reveal paramagnetic behavior down to 2 K with a moment of 8.12 $\mu_B$/Gd atom. As reported previously, the experimentally derived moment of 2.18 $\mu_B$/Ce atom points to a certain amount of Ce4+ in Tl9CeTe6.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/10/4/277/s1, Table S1: Crystallographic data and refinement parameters of Tl9RETe6 in space group I4/mcm with Tl1/RE mixed occupancy on Wyckoff site 4c of the for reasons of comparison, Figure S1: Profile plots for Tl9CeTe6, and Tl9SmTe6 (exp. data and Rietveld fits), Figure S2: Magnetic data for Tl9CeTe6.

Author Contributions: A.I. performed and analyzed the electronic structure calculations. R.S. performed and analyzed the magnetic measurements. T.D. performed and analyzed the powder and single-crystal X-ray data collections, elucidated the crystal structures and supervised the project. All three authors contributed to writing of the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Deutsche Forschungsgemeinschaft (grants Do 590/5 and IS 250/1) in the framework of the priority program 1666 “Topological Insulators”.

Acknowledgments: We are grateful to M. Münch for sample preparations and to A. Bründer for EDX investigations. Open Access Funding by the Publication Fund of the TU Dresden.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wölfing, B.; Kloc, C.; Teubner, J.; Bucher, E. High performance thermoelectric Tl9BiTe6 with an extremely low thermal conductivity. *Phys. Rev. B* 2001, 86, 4350–4353.
2. Yamanaka, S.; Kosuka, A.; Korosaki, K. Thermoelectric properties of Tl₃BiTe₆. J. Alloys Compd. 2003, 352, 275–278. [CrossRef]
3. Guo, Q.; Kleinke, H. Thermoelectric properties of hot-pressed Tl₆LnTe₆ (Ln = La, Ce, Pr, Nd, Sm, Gd, Tb) and Tl₁₀−ₓLaₓTe₆ (0.90 ≤ x ≤ 1.05). J. Alloys Compd. 2015, 630, 37–42. [CrossRef]
4. Shi, Y.; Sturm, C.; Kleinke, H. Chalcogenides as thermoelectric materials. J. Solid State Chem. 2019, 270, 273–279. [CrossRef]
5. Sankar, C.R.; Bangarigadu-Sanasy, S.; Assoud, A.; Kleinke, H. Syntheses, crystal structures and thermoelectric properties of two new thallium tellurides: Tl₄ZrTe₄ and Tl₄HfTe₄. J. Mater. Chem. 2010, 20, 7485–7490. [CrossRef]
6. Bangarigadu-Sanasy, S.; Sankar, R.; Assoud, A.; Kleinke, H. Crystal structures and thermoelectric properties of the series Tl₁₀−ₓLaₓTe₆ with 0.2 ≤ x ≤ 1.15. Dalton Trans. 2011, 40, 862–867. [CrossRef]
7. Kuropatwa, B.A.; Assoud, A.; Kleinke, H. Phase range and physical properties of the thallium tin tellurides Tl₁₀−ₓSnₓTe₆ (x ≤ 2.2). J. Alloys Compd. 2011, 509, 6768–6772. [CrossRef]
8. Sankar, C.R.; Bangarigadu-Sanasy, S.; Kleinke, H. Thermoelectric Properties of TlGd₉ (Q = Se, Te) and Tl₉GdTe₆. J. Electron. Mater. 2012, 41, 1663–1666. [CrossRef]
9. Sankar, C.R.; Bangarigadu-Sanasy, S.; Kleinke, H. Thermoelectric properties of Tl₁₀−ₓLnₓTe₆ with Ln= Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er, and 0.25 ≤ x ≤ 1.32. J. Alloys Compd. 2013, 549, 126–134. [CrossRef]
10. Bhan, S.; Schubert, K. Kristallstruktur von Tl₂Te₃ und Tl₂Te₅. J. Less-Common Met. 1970, 20, 229–235. [CrossRef]
11. Kuropatwa, B.A.; Guo, Q.; Assoud, A.; Kleinke, H. Optimization of the Telluride Tl₁₀−ₓSnₓBi₃Te₆ for the Thermoelectric Energy Conversion. Z. Anorg. Allg. Chem. 2014, 460, 774–780. [CrossRef]
12. Arpino, K.E.; Wallace, D.C.; Nie, Y.F.; Birol, T.; King, P.D.C.; Chatterjee, S.; Uchida, M.; Koohpayeh, S.M.; Ven, J.-J.; Page, K.; et al. Evidence for topologically protected surface states and a superconducting phase in [Tl₄]([Tl₁₀−ₓSnₓ]Te₃) using photoemission, specific heat, and magnetization measurements, and density functional theory. Phys. Rev. Lett. 2014, 112, 017002. [CrossRef] [PubMed]
13. Bhan, S.; Schubert, K. Kristallstruktur von Tl₂Te₃ und Tl₂Te₅. J. Less-Common Met. 1970, 20, 229–235. [CrossRef]
14. Schewe, I.; Böttcher, P.; von Schnering, H.G. The crystal structure of Tl₃Te₃ and its relationship to the Cr₃B₃ type. Z. Kristallogr. 1989, 188, 287–298. [CrossRef]
15. Berg, L.G.; Abdul’manov, A.G. Pseudobinary System Bi₃Te₃–Tl₆BiTe₆. Izv. Akad. Nauk SSSR Neorg. Mater. 1970, 12, 2192–2193.
16. Vosheshov, Y.V.; Gurzan, M.I.; Kish, Z.Z.; Lada, L.V. Phase equilibria in the Ti-Pb-Te system and crystal structure of TlₓBiₓTe₃ and TlₓBi₂Te₄ compounds. Inorg. Mater. 1998, 24, 1265–1269.
17. Doert, T.; Höpfkes, S.; Klein, C.; Böttcher, P. The crystal structures of AgTl₄Te₃ and AgTl₄Te₅. Z. Kristallogr. Suppl. 1991, 3, 52.
18. Brädtmöller, S.; Böttcher, P. Darstellung und Kristallstruktur von SnTl₄Te₃ und PbTl₄Te₃. Z. Anorg. Allg. Chem. 1993, 619, 1155–1160. [CrossRef]
19. Brädtmöller, S.; Böttcher, P. Crystal structure of molybdenum tetrathallium tritelluride, MoTl₄Te₃. Z. Kristallogr. 1994, 209, 75. [CrossRef]
20. Doert, T.; Böttcher, P. Crystal structure of antimony nonathallium hexatelluride, SbTl₆Te₆. Z. Kristallogr. 1994, 209, 96. [CrossRef]
21. Brädtmöller, S.; Böttcher, P. Crystal structure of copper tetrathallium tritelluride, CuTl₄Te₃. Z. Kristallogr. 1994, 209, 97. [CrossRef]
22. Tokura, Y.; Yasuda, K.; Tsukazaki, A. Magnetic topological insulators. Nat. Rev. Phys. 2019, 1, 126–143. [CrossRef]
23. Petricek, V.; Dusek, M.; Palatinus, L. Crystallographic computing system JANA2006: General features. Z. Kristallogr.-Cryst. Mater. 2014, 229, 345–352. [CrossRef]
24. AZTECH; Oxford Instruments: Oxford, UK, 2013.
25. APEX Suite; Bruker-AXS: Madison, WI, USA, 2013.
26. Sheldrick, G.M. (Ed.) SADAB5; Bruker AXS: Karlsruhe, Germany, 2002.
27. DIAMOND 4; Version 4.6.1; Structure Visualization Software; Crystal Impact GbR: Bonn, Germany, 2019.
28. The Elk FP–LAPW Code, Version 1.4.22. Available online: http://elk.sourceforge.net (accessed on 17 March 2019).

29. Shick, A.B.; Liechtenstein, A.I.; Pickett, W.E. Implementation of the LDA+U method using the full-potential linearized augmented plane-wave basis. Phys. Rev. B 1999, 60, 10763. [CrossRef]

30. Bader, R.F.W. Atoms in Molecules; Oxford University Press: Oxford, UK, 1990.

31. Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallogr. 1976, 32, 751–767. [CrossRef]

32. Nordell, K.J.; Miller, G.J. Electronic structure, superconductivity, and substitution patterns in Tl5Te3. J. Alloys Comp. 1996, 241, 51–62. [CrossRef]

33. Blundell, S. Magnetism in Condensed Matter; Oxford University Press: Oxford, UK, 2011.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).