Article

Syntheses, Crystal Structure and Magnetic Properties of Tl_9RETe_6 ($\text{RE} = \text{Ce}, \text{Sm}, \text{Gd}$)

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Abstract: The three compounds Tl_9RETe_6 with $\text{RE} = \text{Ce}, \text{Sm}, \text{Gd}$ were synthesized from the elements at 1020 K. Their isostructural crystal structures are ordered derivatives of the Tl_5Te_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: $9 \text{ Tl}^+ + \text{RE}^{3+} + 6 \text{ Te}^{2-}$. DFT calculations for Tl_9GdTe_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_9CeTe_6 ; no indications for long-range magnetic order was found down to $T = 2 \text{ K}$.

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

1. Introduction

Tl_5Te_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_5Te_3 is known to adopt the In_5Bi_3 type structure (space group $I4/mcm$, $a = 893.0(2) \text{ pm}$, $c = 1258.9(4) \text{ pm}$), with two distinct Tl positions (Tl1 on Wyckoff site $4c$ and Tl2 on $16l$) and two Te positions (Te1 on $4a$, Te2 on $8h$) [12,13]. Several ternary derivatives of the types Tl_9MTe_6 ($M = \text{Sb}, \text{Bi}$), Tl_9RETe_6 ($\text{RE} = \text{rare earth metal}$) and $\text{Tl}_4\text{M}'\text{Te}_3$ ($M' = \text{Cu}, \text{Sn}, \text{Pb}, \text{Mo}$) have been reported [1–11,14–21]. Substitutions have generally been found to occur on Wyckoff site $4c$ preferably. The composition $\text{Tl}_4\text{M}'\text{Te}_3$ could in principle be realized by complete substitution of Tl1 on Wyckoff site $4c$, the composition Tl_9MTe_6 corresponds to a substitution of one-half of the Tl1 atoms. Mixed M/Tl occupancies on the $4c$ site were reported for $\text{Tl}_{10-x}\text{RE}_x\text{Te}_6$ ($\text{RE} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$ and Er , with $0 < x < 1.32$), e.g., [6,9]. Magnetization data for the compounds $\text{Tl}_{10-x}\text{RE}_x\text{Te}_6$, $\text{RE} = \text{Ce}, \text{Pr}, \text{Tb}$, Sm point at paramagnetic behavior in low fields down to $T = 2 \text{ K}$ 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_9RETe_6 could be written as $9 \text{ Tl}^+ + \text{RE}^{3+} + 6 \text{ Te}^{2-}$ 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 Tl1^+ atoms.

The progenitor of the series Tl_5Te_3 has a non-trivial topology of the electronic band structure due to a band inversion between the Tl2 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_9RETe_6 with $\text{RE} = \text{Ce}, \text{Sm}, \text{Gd}$ 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; $\text{CuK}\alpha_1$ 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 XMAX^N (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 $K\alpha$ 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 Tl_9GdTe_6 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 sample of Tl_9CeTe_6 and Tl_9GdTe_6 were carried out with a commercial superconducting quantum interference device (SQUID) magnetometer MPMS (Quantum Design Europe, Darmstadt, Germany) in a temperature range of $300\text{ K} \leq T \leq 2\text{ K}$.

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_9RETe_6 (atom-%), stated are average values from different crystals of each sample.

Element	Tl_9CeTe_6	Tl_9SmTe_6	Tl_9GdTe_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_9CeTe_6 , Tl_9SmTe_6 and Tl_9GdTe_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_9GdTe_6 as example; the positions of the Bragg reflections and the difference plot are shown in the lower part; $\text{CuK}\alpha_1$, $\lambda = 1.54051\text{ \AA}$. Profile R factors: $\text{GOF} = 1.84$, $R_p = 3.81$, $wR_p = 6.08$.

Analyses of the single-crystal data sets of the compounds Tl_9CeTe_6 , Tl_9SmTe_6 and Tl_9GdTe_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 Tl_9SmTe_6). 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 RE^{3+} ions to reside on two crystallographically independent sites, as has been described for SbTl_9Te_6 in a similar way [20]. The symmetry and structure relations between Tl_5Te_3 in space group $I4/mcm$ and those of the title compounds Tl_9RETe_6 ($\text{RE} = \text{Ce}, \text{Sm}, \text{Gd}$) 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 (Tl_9CeTe_6), CSD-427737 (Tl_9GdTe_6) and CSD-427738 (Tl_9SmTe_6). 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 Tl_9RETe_6 .

Chemical Composition	Tl_9CeTe_6	Tl_9SmTe_6	Tl_9GdTe_6
$M_r/\text{g}\cdot\text{mol}^{-1}$, $F(000)$	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 $K\alpha$, 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(8)	1306.56(5)
cell volume/ 10^6 pm^3	1041.48(5)	1026.7(1)	1027.96(6)
density/ $\text{g}\cdot\text{cm}^{-3}$	8.75	8.91	8.92
Abs. coefficient/ mm^{-1}	79.69	81.48	81.75
absorption correction		multi-scan (SADABS [26])	
-	0.289/0.749	0.292/0.746	0.499/0.747
crystal size / mm^3	$0.189 \times 0.057 \times 0.045$	$0.021 \times 0.027 \times 0.043$	$0.075 \times 0.061 \times 0.035$
measurement range	$2.8 \leq \theta \leq 42.6$	$2.8 \leq \theta \leq 34.7$	$2.8 \leq \theta \leq 35.2$
	$-13 \leq h \leq 15$	$-11 \leq h \leq 14$	$-14 \leq h \leq 13$
	$-15 \leq k \leq 15$	$-9 \leq k \leq 14$	$-14 \leq k \leq 11$
	$-15 \leq l \leq 24$	$-20 \leq l \leq 20$	$-17 \leq l \leq 19$
R_{int}	0.0328	0.071	0.030
refinement	JANA2006, full-matrix least squares on F^2 [23]		
reflections, with $I > 3\sigma(I)$, 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
$R_1(\text{obs})$, $wR_2(\text{obs})$	0.031, 0.065	0.035, 0.062	0.026, 0.049
$R_1(\text{all})$, $wR_2(\text{all})$	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)
$\Delta\rho_{\text{min}} / \Delta\rho_{\text{max}}$, $\text{e}/10^6 \text{ pm}^3$	2.57/-2.02	2.02/-3.38	2.29/-2.12

* from powder data

Figure 2. Bärnighausen diagram showing the symmetry relationship between the binary Tl_5Te_3 [14] and the Tl_9RETe_6 title compounds.

As the three title compounds Tl_9CeTe_6 , Tl_9SmTe_6 and Tl_9GdTe_6 are isotypic, the structure description and discussion are exemplified by Tl_9SmTe_6 . The structures of Tl_5Te_3 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 Te1 [15–21] or a perovskite-like arrangement of $TlTe_6$ -octahedra in which the large voids are occupied by Tl_4 -tetrahedra [12]. Figure 3 shows projections of the unit cells of Tl_9SmTe_6 and Tl_5Te_3 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 Tl_9RETe_6 .

Atom	x	y	z	U_{eq} , pm ²
Tl_9CeTe_6				
Ce	0	0	0	170(1)
Tl1	0	0	1/2	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)
Tl_9SmTe_6				
Sm	0	0	0	173(3)
Tl1	0	0	1/2	0273(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)
Tl_9GdTe_6				
Gd	0	0	0	173(3)
Tl1	0	0	1/2	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)

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

A more detailed view on the structures, especially on the $TlTe_6$ and $SmTe_6$ octahedra, however, reveals further differences. The $TlTe_6$ 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.

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

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 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.

Table 4. Selected interatomic distances (pm) of Tl_9RETe_6 .

Tl ₉ CeTe ₆							
Ce–	Te1	315.7(1)	2×	Tl1–	Te1	341.1(1)	2×
	Te2	322.8(1)	4×		Te2	344.4(1)	4×
	Tl2	409.2(1)	8×		Tl2	391.4(1)	8×
Tl2–	Tl2	352.3(1)		Tl2–	Te2	320.0(1)	
		352.8(1)	2×			346.4(1)	
		370.2(1)				347.6(1)	
		Te1	355.2(1)				
			366.6(1)				
Tl ₉ SmTe ₆							
Sm–	Te1	309.9(1)	2×	Tl1–	Te1	343.3(1)	2×
	Te2	317.5(1)	4×		Te2	346.0(1)	4×
	Tl2	405.9(1)	8×		Tl2	391.3(1)	8×
Tl2–	Tl2	350.2(1)		Tl2–	Te2	318.1(1)	
		350.3(1)	2×			343.6(1)	
		362.0(1)				348.7(1)	
		Te1	356.8(1)				
			362.0(1)				
Tl ₉ GdTe ₆							
Gd–	Te1	309.4(1)	2×	Tl1–	Te1	343.9(1)	2×
	Te2	316.9(1)	4×		Te2	346.9(1)	4×
	Tl2	405.7(1)	8×		Tl2	392.0(1)	8×
Tl2–	Tl2	350.1(1)		Tl2–	Te2	318.2(1)	
		350.4(1)	2×			343.1(1)	
		368.2(1)				349.7(1)	
		Te1	357.6(1)				
			361.5(1)				

Tl_5Te_3 , Tl_5Se_3 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 Tl_9RETe_6 , this would result in $9 \text{ Tl}^+ + \text{RE}^{3+} + 6 \text{ Te}^{2-}$. The sizes of the metal coordination octahedra can then be rationalized according to the ionic radii of the respective Tl^+ and RE^{3+} metal ions: 164 pm for Tl^+ , 115 pm for Ce^{3+} , 110 pm for Sm^{3+} and 108 pm for Gd^{3+} , all for octahedral coordination [31]. The smaller TlTe_6 coordination polyhedron in Tl_5Te_3 as compared to those in Tl_9RETe_6 is also understandable: In Tl_5Te_3 one fifth of the Tl atoms (i.e., the Tl atoms on 4c in space group $I4/mcm$) can be considered to be in an intermediate 2+ valence state: $4 \text{ Tl}^+ + \text{Tl}^{2+} + 3 \text{ Te}^{2-}$ [32]. However, the formulation as mixed-valent compound according to $9 \text{ Tl}^+ + \text{Tl}^{3+} + 6 \text{ Te}^{2-}$ is conceivable, yet not supported by crystallographic evidence.

Figure 5. Extended coordination polyhedra for Sm (left) and Tl1 atoms (right): slightly compressed Te_6 octahedra plus Tl_8 cuboid.

Based on the crystallographic data, we perform preliminary spin-polarized band-structure calculations for Tl_9GdTe_6 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, Tl_9GdTe_6 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 $7.4 \mu_B/\text{Gd atom}$. This value is slightly lower than the theoretical moment of $7.98 \mu_B$ for Gd^{3+} [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 .

Figure 6. Full-relativistic spin-polarized band structure of Tl_9GdTe_6 .

Magnetic measurements performed on samples of Tl_9CeTe_6 (Figure S2) and Tl_9GdTe_6 (Figure 7) demonstrate that both compounds are paramagnetic in the temperature interval $2 \text{ K} < T < 300 \text{ K}$ and no long-range magnetic order was established. The Curie–Weiss fit for Tl_9CeTe_6 results in a magnetic moment of $2.18 \mu_B$ per Ce-atom, in accordance with [10]. The values are slightly reduced with respect to the expected value of $2.51 \mu_B$ for a pure Ce^{3+} ($J = 5/2$) system [33] and might point towards a small amount of Ce^{4+} . For Tl_9GdTe_6 , the Curie–Weiss fit yields $8.12 \mu_B$ per Gd atom for the Gd compound in reasonable agreement with the expected value for a $J = 7/2$ system of $7.98 \mu_B$ [33]. Whereas binary Tl_5Te_3 turns superconducting at $T_c = 2.4 \text{ K}$ [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.

Figure 7. Tl_9GdTe_6 magnetic moment versus magnetic field for at $T = 2$ K (left) and magnetic moment vs. temperature for in external fields of 100 Oe (right). The red line depicts the Curie–Weiss fit according to $\chi = A + \frac{C}{T-\theta}$ with A : temperature independent correction term for core diamagnetism, Van Vleck contribution and Pauli paramagnetic contribution, C = Curie temperature, θ = Weiss constant.

4. Conclusions

In contrast to previous investigations, the stoichiometrically substituted tellurides Tl_9CeTe_6 , Tl_9SmTe_6 and Tl_9GdTe_6 were found to adopt an ordered variant of the In_5Bi_3 type, which allows for an adaption of the different metal atom sizes. The compounds crystallize in space group $I4/m$ (no. 87) and the structures can be understood as charge-ordered in accordance with a Zintl-type formula $(\text{TI}^+)_9\text{RE}^{3+}(\text{Te}^{2-})_6$. Spin-polarized DFT calculations for Tl_9GdTe_6 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 Tl_9RETe_6 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 Γ point of the 3D Brillouin zone at ca. 0.2 eV below the Fermi level. Thus, Tl_9GdTe_6 may become a candidate topological material upon p -doping and given a ferromagnetic ordering. The calculated ground state is ferromagnetic with $7.4 \mu_B/\text{Gd-atom}$, however, magnetization measurements reveal paramagnetic behavior down to 2 K with a moment of $8.12 \mu_B/\text{Gd atom}$. As reported previously, the experimentally derived moment of $2.18 \mu_B/\text{Ce atom}$ points to a certain amount of Ce^{4+} in Tl_9CeTe_6 .

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 Tl_9RETe_6 in space group $I4/mcm$ with $\text{Tl1}/\text{RE}$ mixed occupancy on Wyckoff site 4c of the for reasons of comparison, Figure S1: Profile plots for Tl_9CeTe_6 , and Tl_9SmTe_6 (exp. data and Rietveld fits), Figure S2: Magnetic data for Tl_9CeTe_6 .

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.

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