

Article

Revisiting the Zintl-Klemm Concept for $\text{ALn}_2\text{Ag}_3\text{Te}_5$ -Type Alkaline-Metal (A) Lanthanide (Ln) Silver Tellurides

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Abstract: Understanding the bonding nature of solids is decisive, as knowledge of the bonding situation for any given material provides valuable information about its structural preferences and physical properties. Although solid-state tellurides are at the forefront of several fields of research, the electronic structures, particularly their nature of bonding, are typically understood by applying the Zintl-Klemm concept. However, certain tellurides comprise ionic as well as strong (polar) mixed-metal bonds, in obvious contrast to the full valence-electron transfers expected by Zintl-Klemm's reasoning. How are the valence-electrons really distributed in tellurides containing ionic as well as mixed-metal bonds? To answer this question, we carried out bonding and Mulliken as well as Löwdin population analyses for the series of $\text{ALn}_2\text{Ag}_3\text{Te}_5$ -type tellurides (A = alkaline-metal; Ln = lanthanide). In addition to the bonding analyses, we provide a brief description of the crystal structure of this particular type of telluride, using the examples of $\text{RbLn}_2\text{Ag}_3\text{Te}_5$ (Ln = Ho, Er) and $\text{CsLn}_2\text{Ag}_3\text{Te}_5$ (Ln = La, Ce), which have been determined for the first time.

Keywords: tellurides; polar intermetallics; Mulliken and Löwdin charges

1. Introduction

In the quest for task-specific solid-state materials, computational materials design is of great relevance, because these density-functional-theory-based approaches provide valuable information regarding thermodynamic quantities and, furthermore, the physical properties of materials [1]. As part of the quantum-chemical examinations of solid-state materials, the nature of bonding is typically explored, as general valence-electron rules often do not apply [2]. However, elucidating the nature of bonding is decisive for designing solid-state materials and their properties. Namely, the bond energy evidently contributes to the total electronic (ground state) energy, providing conclusive hints to the structural preferences of materials [3,4], while the bonding characteristics of the states near the Fermi level of a given material influence its physical properties. For instance, the latter circumstance becomes fully apparent regarding the Fermi level characteristics of certain chalcogenide superconductors [5,6], the magnetic ground state of transition-metals [7], and the optical as well as the electric properties of phase-change materials [8,9], to name but a few.

One particular group of intermetallics that is subject to the quest for (unprecedented) task-specific materials is the family of the tellurides, because tellurides are at the cutting edge of many fields of research, including thermoelectrics [10,11], phase-change data-storage materials [12,13], and topological insulators [14]. In the light of such relevance for research and technical applications, one could also expect that the nature of bonding in tellurides is typically examined employing first-principles-based approaches; yet, the electronic structures, particularly the nature of bonding, in many tellurides are frequently (and simplistically) interpreted by applying the Zintl-Klemm concept rather than first-principles-based bonding analyses [15]. More recent research [16–18] on the electronic structures of certain tellurides, however, demonstrated that such Zintl-Klemm pictures should be taken with a pinch of salt. In fact, examining the electronic structures of (active-metal) transition-metal tellurides (active-metal = group I and III elements) revealed that the bonding nature in these tellurides is dominated by strong transition-metal–tellurium interactions beside minor transition-metal–transition-metal or tellurium–tellurium interactions. Because the transition-metal–tellurium interactions in these tellurides exhibited attributes of strong mixed-metal bonds, it was concluded that these tellurides should be assigned to the groups of polar intermetallics [19,20] rather than the Zintl phases.

Further research on the nature of bonding in a quaternary $ALn_2Ag_3Te_5$ -type telluride [18] (A = alkaline-metal; Ln = lanthanide), which also comprised strong mixed-metal transition-metal–tellurium interactions, showed that the alkaline-metal–tellurium interactions appear as ionic bonds. Because the alkaline-metal–tellurium contacts should be viewed as ionic contacts while the Zintl-Klemm approach should be considered with concern, how can the charge of the alkaline-metal be determined? Again, first-principles-based means help us to answer this question. Namely, more recent research [21] demonstrated that Mulliken and Löwdin charges can be directly calculated from plane-wave-based electronic structure computations of solid-state materials. Herein, we present the outcome of the Mulliken and Löwdin population analysis, which has been conducted for a representative of the $ALn_2Ag_3Te_5$ -type and compared to the results of a (chemical) bonding analysis. Prior to the examinations of the electronic structures, we will also briefly describe the structural features of this particular type of structure for the examples of the previously unknown $RbLn_2Ag_3Te_5$ (Ln = Ho, Er) and $CsLn_2Ag_3Te_5$ (Ln = La, Ce).

2. Results and Discussion

To probe the charge distributions in a telluride, which is considered to comprise both ionic and mixed-metal bonds, we conducted chemical bonding as well as Mulliken and Löwdin population analyses for the example of $CsCe_2Ag_3Te_5$. All tellurides were obtained from reactions of the corresponding rare-earth elements, silver and tellurium in the presence of the respective alkaline-metal chlorides that were employed as reactive fluxes [22] (see Section 3.1). A phase analysis was accomplished based on the powder X-ray diffraction patterns collected for the samples, and it revealed that the tellurides were obtained in considerable yields; yet, all tellurides were accompanied by by-products that were binary lanthanide tellurides, Ag_2Te , $CsAg_5Te_3$, and an unknown phase (see Figure 1). The lattice parameters of the holmium-containing telluride have been recently reported elsewhere [18], while the crystal structures of the previously unknown $RbEr_2Ag_3Te_5$ and $CsLn_2Ag_3Te_5$ (Ln = La, Ce) have been determined for the first time (see Tables 1 and 2).

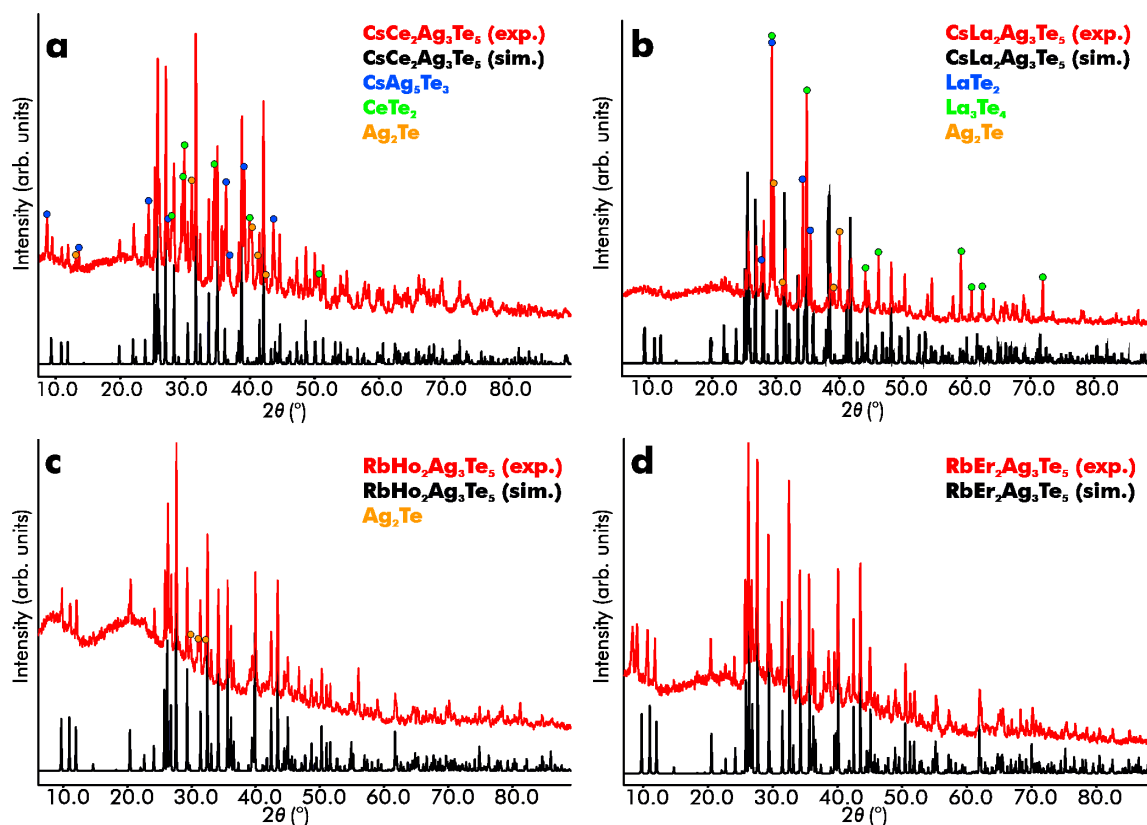


Figure 1. Experimental and theoretical powder X-ray diffraction patterns of (a) $\text{CsCe}_2\text{Ag}_3\text{Te}_5$, (b) $\text{CsLa}_2\text{Ag}_3\text{Te}_5$, (c) $\text{RbHo}_2\text{Ag}_3\text{Te}_5$, and (d) $\text{RbEr}_2\text{Ag}_3\text{Te}_5$; reflections arising from side-products [23–27] are marked by the diverse circles. In the experimental powder X-ray diffraction pattern of the $\text{RbEr}_2\text{Ag}_3\text{Te}_5$ -containing sample, there are also reflections (below 10° and between 30° and 40°), which could not be assigned to the quaternary telluride, and originate from an unknown phase.

2.1. Structural Details

An inspection of the unit-cell volumes for the herein and previously reported $\text{ALn}_2\text{Ag}_3\text{Te}_5$ -type tellurides ($A = \text{Rb}$, $\text{Ln} = \text{Pr}$, Nd , Sm , Gd – Er ; $A = \text{Cs}$, $\text{Ln} = \text{La}$ – Nd , Sm , Gd – Er) [18,28] shows that the volumes decrease, while the atomic number of the rare-earth elements increases. For instance, a comparison of the lattice parameters of $\text{CsLn}_2\text{Ag}_3\text{Te}_5$ ($\text{Ln} = \text{La}$, Ce) to those of the isostructural $\text{CsLn}_2\text{Ag}_3\text{Te}_5$ ($\text{Ln} = \text{Pr}$, Nd , Sm , Gd – Er) reveals that the molar volumes of the lanthanum- and cerium-containing tellurides are slightly larger than those of the remaining tellurides (see Figure 2). On the contrary, the unit-cell volumes of $\text{RbLn}_2\text{Ag}_3\text{Te}_5$ ($\text{Ln} = \text{Ho}$, Er) are smaller than those of the isostructural $\text{RbLn}_2\text{Ag}_3\text{Te}_5$ ($\text{Ln} = \text{Pr}$, Nd , Sm , Gd , Tb , Dy). This outcome is a consequence of the lanthanide contraction, which implicates a decrease in the effective atomic radii of the rare-earth elements with an increase in the atomic numbers. Notably, the decrease in the volumes is more evident among the tellurides containing lighter lanthanides ($\text{Ln} = \text{La}$ – Sm) than among the tellurides composed of heavier lanthanides ($\text{Ln} = \text{Gd}$ – Er)—a circumstance that has also been previously [29] encountered for rare-earth-metal-containing intermetallics.

The crystal structures of the $\text{ALn}_2\text{Ag}_3\text{Te}_5$ -type tellurides (see Figure 3) are composed of tunnels, which are constructed by tellurium atoms and encompass the alkaline-metal, rare-earth metal, and silver atoms. The alkaline-metal atoms occupy the centers of bicapped trigonal tellurium prisms, whose triangular bases are condensed to ${}^\infty[\text{A@Te}_8]$ chains propagating parallel to the a axis. Each $[\text{A@Te}_8]$ unit shares six common edges with the $[\text{Ln@Te}_6]$ octahedra of the four nearest neighboring ${}^\infty[\text{Ln@Te}_6]$ double chains, in which the $[\text{Ln@Te}_6]$ octahedra within and between a particular ${}^\infty[\text{Ln@Te}_6]$ single chain are condensed via common edges.

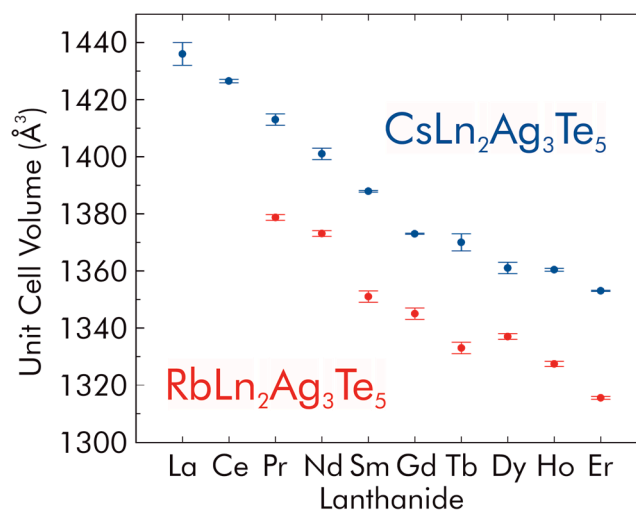


Figure 2. Overview of the unit-cell volumes of the herein and previously reported [18,28] $ALn_2Ag_3Te_5$ -type tellurides ($A = Rb, Ln = Pr, Nd, Sm, Gd-Er$; $A = Cs, Ln = La-Nd, Sm, Gd-Er$).

Table 1. Details of the crystal structure investigations and refinements of $RbLn_2Ag_3Te_5$ ($Ln = Ho, Er$) and $CsLn_2Ag_3Te_5$ ($Ln = La, Ce$).

Formula	$RbHo_2Ag_3Te_5$	$RbEr_2Ag_3Te_5$	$CsLa_2Ag_3Te_5$	$CsCe_2Ag_3Te_5$
form wt.	1376.94	1381.60	1372.34	1374.76
space group	$Cmcm$ (no. 63)			
a (Å)	4.517(2)	4.493(1)	4.662(7)	4.647(1)
b (Å)	16.096(6)	16.069(4)	16.21(2)	16.223(4)
c (Å)	18.256(7)	18.220(4)	19.00(3)	18.921(5)
volume (Å ³)	1327.4(9)	1315.5(5)	1436(4)	1426.5(6)
Z	4			
density (calc.), g/cm ³	6.890	6.976	6.348	6.401
μ (mm ⁻¹)	30.490	31.494	22.247	22.785
$F(000)$	2288	2296	2280	2288
θ range (°)	2.231–26.563	2.236–25.216	2.144–25.352	2.153–31.006
index ranges	$-5 \leq h \leq 5$	$-5 \leq h \leq 5$	$-4 \leq h \leq 5$	$-6 \leq h \leq 6$
	$-20 \leq k \leq 19$	$-18 \leq k \leq 18$	$-17 \leq k \leq 19$	$-15 \leq k \leq 23$
	$-19 \leq l \leq 22$	$-21 \leq l \leq 13$	$-22 \leq l \leq 22$	$-26 \leq l \leq 27$
reflections collected	4259	3070	4046	5769
independent reflections	809	701	769	1236
refinement method	full-matrix least-squares on F^2			
data/restraints/parameters	809/0/37	701/0/37	769/0/37	1236/0/37
goodness-of-fit on F^2	1.16	1.13	0.89	1.06
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.046$; $wR_2 = 0.099$	$R_1 = 0.057$; $wR_2 = 0.144$	$R_1 = 0.056$; $wR_2 = 0.129$	$R_1 = 0.026$; $wR_2 = 0.055$
	$R_1 = 0.056$; $wR_2 = 0.102$	$R_1 = 0.061$; $wR_2 = 0.146$	$R_1 = 0.094$; $wR_2 = 0.145$	$R_1 = 0.038$; $wR_2 = 0.056$
R_{int}	0.073	0.074	0.173	0.042
largest difference peak and hole, e-/Å ³	2.18 and −6.96	4.02 and −5.74	1.91 and −3.78	1.54 and −1.90

Table 2. Atomic positions and equivalent displacement parameters for $\text{RbLn}_2\text{Ag}_3\text{Te}_5$ (Ln = Ho, Er) and $\text{CsLn}_2\text{Ag}_3\text{Te}_5$ (Ln = La, Ce).

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{\AA}^2$
RbHo₂Ag₃Te₅					
Ho1	8 <i>f</i>	0	0.1915(1)	0.4050(1)	0.0148(3)
Te2	8 <i>f</i>	$\frac{1}{2}$	0.0632(1)	0.3786(1)	0.0165(3)
Te3	8 <i>f</i>	0	0.1768(1)	0.5721(1)	0.0142(3)
Te4	4 <i>c</i>	0	0.2616(1)	$\frac{1}{4}$	0.0161(4)
Ag5	8 <i>f</i>	$\frac{1}{2}$	0.0835(1)	0.5330(1)	0.0263(4)
Ag6	4 <i>c</i>	$\frac{1}{2}$	0.1638(1)	$\frac{1}{4}$	0.0274(5)
Rb7	4 <i>c</i>	0	−0.0572(1)	$\frac{1}{4}$	0.0262(6)
RbEr₂Ag₃Te₅					
Er1	8 <i>f</i>	0	0.1919(1)	0.4049(1)	0.0150(4)
Te2	8 <i>f</i>	$\frac{1}{2}$	0.0640(1)	0.3789(1)	0.0162(5)
Te3	8 <i>f</i>	0	0.1772(1)	0.5718(1)	0.0142(5)
Te4	4 <i>c</i>	0	0.2620(1)	$\frac{1}{4}$	0.0149(5)
Ag5	8 <i>f</i>	$\frac{1}{2}$	0.0828(1)	0.5338(1)	0.0267(6)
Ag6	4 <i>c</i>	$\frac{1}{2}$	0.1638(2)	$\frac{1}{4}$	0.0261(7)
Rb7	4 <i>c</i>	0	−0.0569(2)	$\frac{1}{4}$	0.0267(8)
CsLa₂Ag₃Te₅					
La1	8 <i>f</i>	0	0.1910(1)	0.4064(1)	0.0197(5)
Te2	8 <i>f</i>	$\frac{1}{2}$	0.0582(1)	0.3798(1)	0.0214(6)
Te3	8 <i>f</i>	0	0.1699(1)	0.5730(1)	0.0203(6)
Te4	4 <i>c</i>	0	0.2540(2)	$\frac{1}{4}$	0.0222(7)
Ag5	8 <i>f</i>	$\frac{1}{2}$	0.0860(2)	0.5289(2)	0.0302(7)
Ag6	4 <i>c</i>	$\frac{1}{2}$	0.1598(3)	$\frac{1}{4}$	0.0344(10)
Cs7	4 <i>c</i>	0	−0.0596(2)	$\frac{1}{4}$	0.0284(8)
CsCe₂Ag₃Te₅					
Ce1	8 <i>f</i>	0	0.1908(1)	0.4064(1)	0.0138(1)
Te2	8 <i>f</i>	$\frac{1}{2}$	0.0591(1)	0.3801(1)	0.0150(1)
Te3	8 <i>f</i>	0	0.1718(1)	0.5730(1)	0.0133(1)
Te4	4 <i>c</i>	0	0.2539(1)	$\frac{1}{4}$	0.0156(2)
Ag5	8 <i>f</i>	$\frac{1}{2}$	0.0860(1)	0.5296(1)	0.0241(2)
Ag6	4 <i>c</i>	$\frac{1}{2}$	0.1597(1)	$\frac{1}{4}$	0.0271(2)
Cs7	4 <i>c</i>	0	−0.0594(1)	$\frac{1}{4}$	0.0224(2)

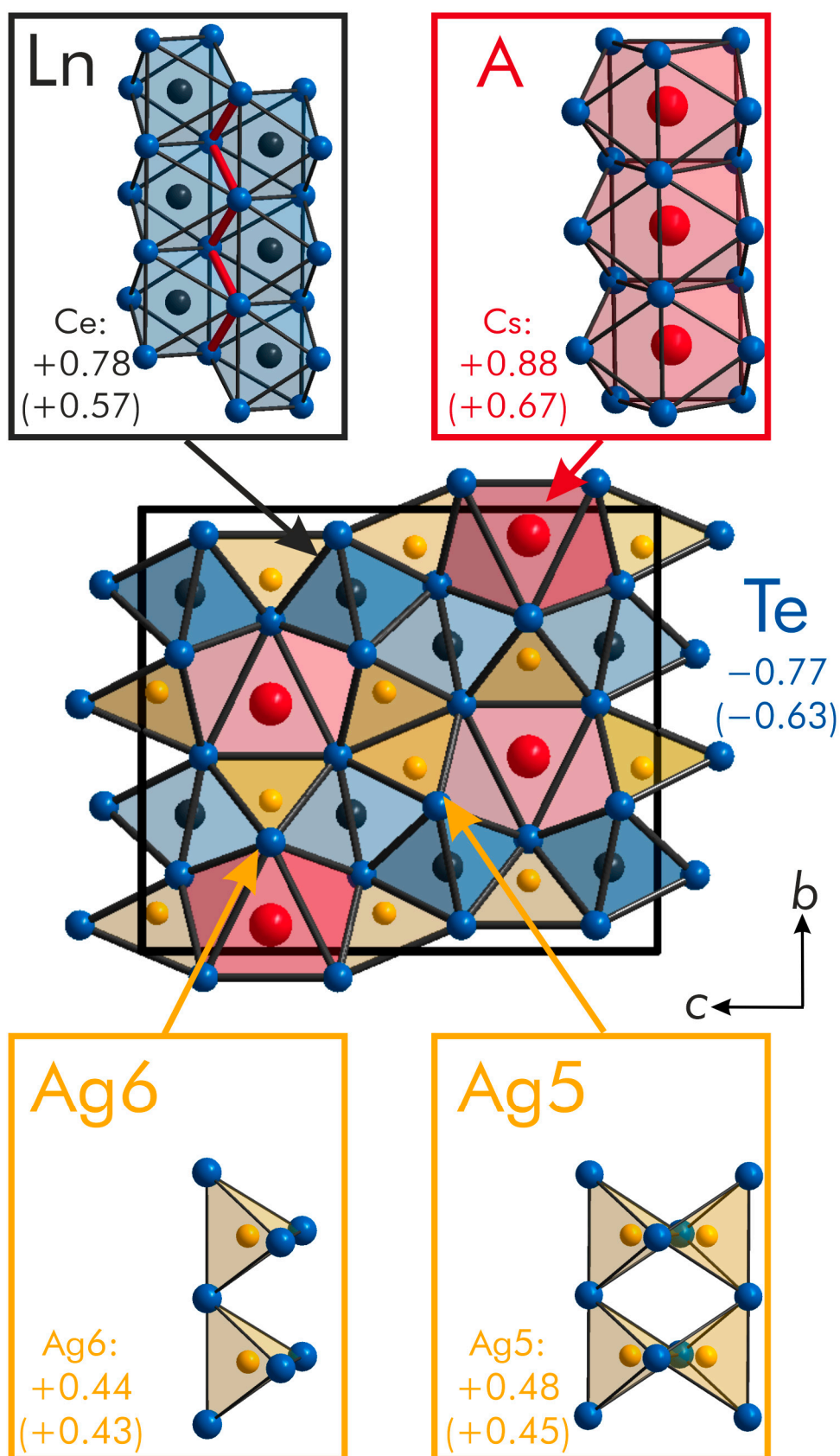


Figure 3. Representation of the crystal structure of the $ALn_2Ag_3Te_5$ -type tellurides: the diverse types of tellurium polyhedra surrounding the alkaline-metal (A), lanthanide (Ln), and silver atoms are shown in the insets, also including the Mulliken and Löwdin charges (in parentheses) which have been calculated for $CsCe_2Ag_3Te_5$. The Mulliken (and Löwdin) charges of tellurium, which vary by ± 0.01 (and ± 0.02) for the different tellurium positions, represent the average charge distribution.

All silver atoms occupy the centers of the tellurium tetrahedra, which are condensed to linear ${}^1_{\infty}[\text{Ag@Te}_4]$ chains, but there are two different types of ${}^1_{\infty}[\text{Ag@Te}_4]$ chains in the crystal structure of the $\text{ALn}_2\text{Ag}_3\text{Te}_5$ -type tellurides (see Figure 3). Each $[\text{Ag@Te}_4]$ tetrahedron comprising a silver atom on Wyckoff position 8f shares two common vertices with the two nearest neighboring $[\text{Ag@Te}_4]$ units within one ${}^1_{\infty}[\text{Ag@Te}_4]$ chain and a common edge with a $[\text{Ag@Te}_4]$ tetrahedron of an adjoining ${}^1_{\infty}[\text{Ag@Te}_4]$ chain, to form ${}^1_{\infty}[\text{Ag@Te}_4]$ double chains. On the contrary, each $[\text{Ag@Te}_4]$ tetrahedron enclosing the silver atoms on Wyckoff site 4c has just two vertices in common with the two adjacent $[\text{Ag@Te}_4]$ units, such that these $[\text{Ag@Te}_4]$ units are condensed to ${}^1_{\infty}[\text{Ag@Te}_4]$ single chains. Furthermore, each ${}^1_{\infty}[\text{Ag@Te}_4]$ single chain is connected via common tellurium vertices to two ${}^1_{\infty}[\text{Ag@Te}_4]$ double chains. A closer inspection of the ${}^1_{\infty}[\text{Ag@Te}_4]$ double chains reveals the presence of remarkably short Ag–Ag separations (e.g. $d(\text{Ag}–\text{Ag}) = 3.005(1)\text{\AA}$ in $\text{CsCe}_2\text{Ag}_3\text{Te}_5$), which are typically indicative of Ag–Ag bonds. Indeed, more recent research [18] on the electronic structure of an $\text{ALn}_2\text{Ag}_3\text{Te}_5$ -type telluride showed that such homoatomic interactions are of a net bonding character.

In summary, the crystal structures of the $\text{ALn}_2\text{Ag}_3\text{Te}_5$ -type tellurides are composed of linear ${}^1_{\infty}[\text{A@Te}_8]$, ${}^1_{\infty}[\text{Ln@Te}_6]$, and ${}^1_{\infty}[\text{Ag@Te}_4]$ chains propagating parallel to the a axis. The short Ag–Ag distances within the ${}^1_{\infty}[\text{Ag@Te}_4]$ double chains indicate the presence of Ag–Ag bonds, which are unexpected within a Zintl-Klemm treatment, leading to the electron-precise description of $(\text{A}^+)(\text{Ln}^{3+})_2(\text{Ag}^+)_3(\text{Te}^{2-})_5$. Indeed, such a Zintl-Klemm picture is oversimplistic because more recent research [18] on the nature of bonding for this particular type of telluride revealed strong mixed-metal interactions for the Ln–Te and Ag–Te contacts. As the A–Te interactions were considered to be rather ionic, one may therefore question the valence-electron distribution in these tellurides. To answer this, we carried out chemical bonding and Mulliken as well as Löwdin population analyses for the example of $\text{CsCe}_2\text{Ag}_3\text{Te}_5$.

2.2. Electronic Structure Computations, Chemical Bonding and Population Analyses

An inspection of the densities-of-states (DOS) curves for $\text{CsCe}_2\text{Ag}_3\text{Te}_5$ shows that the occupied states close to the Fermi level, E_F , arise to a large extent from the Ag-4d and Te-5p orbitals with minor contributions from the Ce-5d orbitals (Figure 4). This outcome suggests that the aforementioned orbitals mainly contribute to the bonding interactions, while the depletion of the Cs-6s orbitals (not shown in Figure 4) reflects the role of cesium as an electron-donor. This circumstance becomes even clearer from a bonding analysis that has been accomplished based on the projected crystal orbital Hamilton populations (–pCOHP) and their respective integrated values (–IpCOHP; Figure 4). In addition, the cumulative –IpCOHP/cell values, i.e., the sum of all –IpCOHP/bond values for a particular sort of interatomic interaction, were projected as percentages of the net bonding capacity—a procedure [30] that has been largely employed to evaluate the roles of different interactions in a given solid-state material.

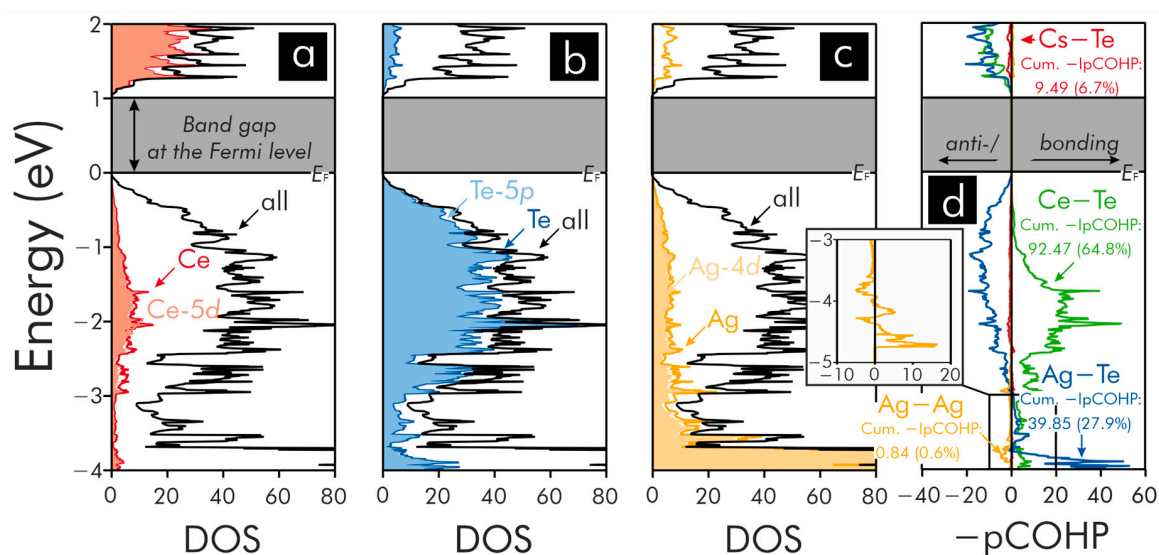


Figure 4. Densities-of-states (DOS) curves and projected crystal orbital Hamilton populations (pCOHP) of $\text{CsCe}_2\text{Ag}_3\text{Te}_5$: the lower and upper black horizontal lines indicate the valence band maximum and conduction band minimum, respectively, while the total, atom- and orbital-projected DOS curves are shown in (a–c). The orbital-projected DOS curves correspond to those states providing the largest contributions to the occupied states near E_F . The Ag–Ag –pCOHP are shown in the inset for a better representation (d).

An examination of the –pCOHP curves for $\text{CsCe}_2\text{Ag}_3\text{Te}_5$ reveals that the Cs–Te interactions correspond to smaller $\langle -\text{IpCOHP}/\text{bond} \rangle = 0.297$ eV relative to those of the Ce–Te ($\langle -\text{IpCOHP}/\text{bond} \rangle = 1.926$ eV) and Ag–Te ($\langle -\text{IpCOHP}/\text{bond} \rangle = 0.830$ eV) contacts. Accordingly, it could be inferred that the majority of the covalent interactions reside between the Ce–Te and Ag–Te interactions. This outcome becomes even clearer from a comparison of the percentage contributions to the net bonding capabilities: although the number of Cs–Te contacts per cell (32) is nearly similar to those of the Ag–Te (48) and Ce–Te (48), the latter interactions correspond to much higher $\langle -\text{IpCOHP}/\text{bond} \rangle$ values, and hence higher percentages, than the Cs–Te interactions. In accordance with previous research [31] on cesium-containing polar intermetallics, such small $\langle -\text{IpCOHP}/\text{bond} \rangle$ values point to less populated Cs–Te states due to the electron-donor character of Cs, while the Ce–Te and Ag–Te interactions may be regarded as (polar) mixed-metal bonds. This outcome is also in contrast to a full electron transfer according to Zintl-Klemm, proposing a valence-electron distribution of $(\text{Cs}^+)(\text{Ce}^{3+})_2(\text{Ag}^+)_3(\text{Te}^{2-})_5$. The absence of a full transfer of valence-electrons, as expected by Zintl-Klemm, is also given by the Mulliken and Löwdin charges (Figure 3). Namely, the calculated charges for cesium agree well with those predicted by the Zintl-Klemm concept, while the charges computed for silver, cerium, and tellurium are much lower.

Applying the Zintl-Klemm concept would not indicate any Ag–Ag bonding interactions within the ${}^1_{\infty}[\text{Ag@Te}_4]$ double chains; the short Ag–Ag distances, however, which have been observed for the ${}^1_{\infty}[\text{Ag@Te}_4]$ double chains, scale in the same range as those typically expected [32] for Ag–Ag bonds. Indeed, an integration of the Ag–Ag –pCOHP curves reveals a net bonding character for these interactions, yet the Ag–Ag $\langle -\text{IpCOHP} \rangle$ values are smaller than those of the Ag–Te and Ce–Te separations, because the former interactions change from bonding to antibonding states below E_F —a common feature [33] of d^{10} – d^{10} closed-shell interactions.

3. Materials and Methods

3.1. Syntheses

RbLn₂Ag₃Te₅ (Ln = Ho, Er) and CsLn₂Ag₃Te₅ (Ln = La, Ce) were obtained from reactions of silver (Alfa[®], Haverhill, MA, USA, ≥ 99.99%), tellurium (Merck[®], Darmstadt, Germany, > 99%), and the respective rare-earth elements (smart-elements[®], Vienna, Austria, La: 99.9%, Ce: 99.9%, Ho: 99.99%, Er: 99.95%) in the presence of the corresponding alkaline-metal chlorides (Sigma Aldrich[®], St. Louis, Mo, USA, RbCl: 99.8%; VWR[®], Radnor, PA, USA, CsCl: ≥ 99.5%). The alkaline-metal chlorides were used as reactive fluxes [34], while powders of the rare-earth elements were obtained from filing larger ingots, whose surfaces were polished prior to every use. Due to the sensitivity of the rare-earth elements to air and moisture, all reactants were stored and handled under a dry argon atmosphere within a glove box (MBraun[®], Garching, Germany; O₂ < 0.1 ppm by volume; H₂O < 0.3 ppm by volume). Mixtures of about 300 mg total weight were first finely ground and then loaded in one-side-closed silica tubes, which were subsequently flame-sealed under a dynamic vacuum of at least $2 \cdot 10^{-3}$ mbar. The samples were heated employing computer-controlled tube furnaces and the following temperature programs: RbLn₂Ag₃Te₅ (Ln = Ho, Er): heat to 850 °C with a rate of 80 °C/h, hold at that temperature for five days, cool to 350 °C with a rate of 2 °C/h, and equilibrate to room temperature within three hours; CsLn₂Ag₃Te₅ (Ln = La, Ce): heat to 900 °C with a rate of 80 °C/h, keep that temperature for 120 h, slowly cool to 350 °C with rate of 5 °C/h, and equilibrate to room temperature within four hours. The excess alkaline-metal chlorides were removed with methanol, and the products were grey powders containing small crystals. Phase analyses based on powder X-ray diffraction patterns of the samples (see 3.2.) revealed that the tellurides were obtained in considerable yields (see Figure 1).

3.2. X-Ray Diffractions Studies and Crystal Structure Determinations

To determine the yields of RbLn₂Ag₃Te₅ (Ln = Ho, Er) and CsLn₂Ag₃Te₅ (Ln = La, Ce) and possible side-products, sets of powder X-ray diffraction patterns were collected for the obtained samples and compared to those simulated for RbLn₂Ag₃Te₅ (Ln = Ho, Er) and CsLn₂Ag₃Te₅ (Ln = La, Ce) and plausible side-products. To do this, the samples were first ground, then dispersed on Mylar sheets, which were equipped with grease and fixed between split aluminum rings, and finally transferred to a STOE[®] StadiP diffractometer (Stoe[®] & Cie, Darmstadt, Germany; area detector; Cu Kα₁ radiation; λ = 1.54059 Å). The sets of powder X-ray diffraction data were collected at room temperature using the WinXPow [35] software package that was also employed for further processing of the raw data. In addition to the measurements, the phase analyses were carried out with the Match! [36] code.

The crystal structures of RbLn₂Ag₃Te₅ (Ln = Ho, Er) and CsLn₂Ag₃Te₅ (Ln = La, Ce) were determined based on single-crystal X-ray intensity datasets. Prior to the collections of the sets of single-crystal X-ray intensity data, samples were selected from the bulk materials, fixed on capillaries with grease, and transferred to a Bruker[®] APEX CCD diffractometer (Bruker Inc.[®], Madison, WI, USA, Mo Kα radiation; λ = 0.71073 Å). The diffractometer was utilized for initial examinations of the quality of the selected samples and the collections of the sets of single-crystal X-ray intensity data at room temperature. The integrations of the raw datasets and multi-scan absorption corrections were carried out using the programs SAINT+ and SADABS, respectively [37]. Detecting the reflection conditions of the single-crystal X-ray intensity data sets was achieved with the XPREP [38] code and pointed to space group *Cmcm* (no. 63) for the four tellurides. The structures were solved using direct methods (SHELXS-97 [39]) and refined in full matrix least-squares on *F*² (SHELXL-97 [39,40]), which also included anisotropic atomic displacement parameters. CCDC 1975970, 1975983, 1975984, and 1975985 contain the crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-Mail: deposit.ccdc.cam.ac.uk.

3.3. Computational Details

Full structural optimizations, which included lattice parameters and atomic positions, and all electronic (band) structure computations of $\text{CsCe}_2\text{Ag}_3\text{Te}_5$, were carried out with the projector augmented wave (PAW) method [41] within the Vienna ab initio simulation package [42–46] (VASP). Correlation and exchange in all computations were described by the generalized gradient approximation of Perdew, Burke, and Ernzerhof (GGA–PBE [47]), and the energy cutoff of the plane-wave basis set was 500 eV. A mesh of $12 \times 3 \times 3$ k-points was used to sample the first Brillouin zones, while all calculations were expected to be converged, as the energy differences between two iterative steps fell below 10^{-8} (and 10^{-6}) eV/cell for the electronic (and ionic) relaxations.

The nature of bonding in $\text{CsCe}_2\text{Ag}_3\text{Te}_5$ was determined based on the projected crystal orbital Hamilton populations (pCOHP) [48], and Mulliken as well as Löwdin population analysis. In the former approach, which is a variant of the COHP technique [30,49], the off-site DOS are weighted with the respective Hamiltonian matrix elements to reveal bonding, non-bonding, and antibonding interactions. The Mulliken and Löwdin charges are obtained by subtracting the gross population of a given type of atom from its number of valence-electrons [21]. To obtain both the pCOHP and the Mulliken as well as Löwdin charges, the delocalized nature of the electronic structure within the plane-waves representation was transformed into a local one using all-electron contracted Slater-type orbitals. This projective transformation was accomplished employing the Local Orbital Basis Suite Towards Electronic-Structure Reconstruction code (LOBSTER) [48–51], in which the crystal wave functions are constructed from the outcome of the plane wave-based computations with the aid of a transfer matrix.

4. Conclusions

Tellurides have attracted enormous attention among chemists, physicists, and engineers, because many tellurides are at the cutting edge of several fields of research and technologies. To understand and, furthermore, design their properties, it is mandatory to provide an insight into their electronic structures. In doing so, we prototypically explored the electronic structure and bonding nature of an $\text{ALn}_2\text{Ag}_3\text{Te}_5$ -type telluride. The crystal structure of this particular type of telluride was examined taking the previously unknown $\text{RbLn}_2\text{Ag}_3\text{Te}_5$ ($\text{Ln} = \text{Ho}, \text{Er}$) and $\text{CsLn}_2\text{Ag}_3\text{Te}_5$ ($\text{Ln} = \text{La}, \text{Ce}$), which are composed of tunnels that are assembled by the tellurium atoms and encompass the alkaline-metal, lanthanide, and silver atoms. From a bonding analysis of the cerium-containing telluride, it is clear that the Ce–Te and Ag–Te interactions should be described as polar mixed-metal bonds, while the Cs–Te interactions should be depicted as ionic. An analysis of the Mulliken and Löwdin charges for $\text{CsCe}_2\text{Ag}_3\text{Te}_5$ reveals that the charges computed for cerium, silver, and tellurium significantly differ from those charges predicted by the Zintl-Klemm concept. Accordingly, it is rather disputable to describe the electronic structures of $\text{ALn}_2\text{Ag}_3\text{Te}_5$ -type tellurides by means of the latter framework.

Author Contributions: K.E. and F.C.G. conducted the syntheses and solutions as well as refinements of the crystal structures, while the electronic structure computations were carried out by K.S.F. S.S. independently designed the project, which was supervised by R.D. and S.S. The manuscript was written with input from all authors (K.E., K.S.F., F.C.G., R.D., and S.S.), who approved the final version of the manuscript. All authors have read and agreed to the published version of the manuscript.

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