Reduced Ternary Rare-Earth-Transition Metal Tellurides for the Smaller Rare-Earth Elements. An Exploration and an Explanation of the Marked Stability Differentiation among the Rare-Earth Elements in These Phases

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Dedicated to Professor Gerd Meyer on the Occasion of His 60th Birthday

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Abstract. The existence of further metal-rich condensed cluster compounds in R-Z-Te systems has been synthetically explored for R = Sc, Y, Pr, Dy, Er, Tm, Yb, Lu and, mainly, Z = Ru, Rh, Pd, Ag, Ir, Pt, Au. Ten new examples of orthorhombic $\text{Er}_7\text{Ni}_2\text{Te}_2$ -type (*Imm2*) have been identified and that for $\text{Dy}_7\text{Ir}_2\text{Te}_2$ has been refined. Seven new examples of other ternary structure types plus X-ray powder pattern evidence for 14 unknown phases have also been identified. To date the family of ternary R-Z-Te phases ap-

Introduction

The rare-earth elements R (Sc, Y, La-Lu) have in recent decades provided a notable variety of otherwise unprecedented metal-rich cluster phases in which the clusters are centered by a late transition metal heteroatom Z. The cluster phases were first identified among the halides, initially for zirconium and later with the rare-earth metals, as more or less stoichiometric cluster phases with carbon, nitrogen, oxygen, boron, silicon, etc. interstitials (Z), often as common impurity atoms [1, 2]. The fundamental cluster centering condition appears to originate with the otherwise electron-poor character of the M_6X_{12} cluster shells (M = Zr, R; X = Cl, I) relative to the familiar tantalum and niobium analogues [3]. Clusters of the earlier metals are naturally larger and afford more room for the interstitials. The centering of these nonmetal components also continues the theme of more-or-less alternating metal-nonmetal shells. The added bonding, principally via nd on M and s and p orbitals on the interstitial, certainly contributes to the overall sta-

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[b] Ames Laboratory and Department of Chemistry Iowa State University 353 Spedding Hall Ames, IA 50011 USA pears to be limited to those for R = Sc, Y, and Dy-Lu, a trend that is parallel to but more emphatic than those variations found among parallel cluster halide systems. Stability trends among the halide and especially the telluride series follow the I1 + I2 sums for the *R* elements well, the larger values of which are considered to reflect better mixing of *R* and *Z* valence *d* orbitals in the more stable phases.

bility of these phases. Condensation of the rare-earth-metal clusters to chain, sheet, or network structures in various systems naturally follows a lower number of valence electrons and decreases of X:M reaction proportions.

A substantial advance in the concepts of this solid state cluster chemistry occurred with the discovery that both rare-earth metal (and some zirconium) cluster halides could be alternatively centered by metal atoms instead, namely, a considerable number of the later transition metals, viz., 3d-5d metals in groups 7-11 [4, 5]. Orbital bonding schemes in such discrete clusters differed from those for centered nonmetals mainly in the introduction of metal dorbitals, but the occurence of such diverse examples of heteroatomic R-Z intermetal bonding was novel and significant. This feature appears to follow on earlier general concepts developed by Brewer and co-workers [6] regarding the particularly strong bonding present in alloys between early and late transition metals. The dependencies of stability of particular compositions and structure types on the locations of R and Z in the periodic Table are not well studied or clear, but Mullikan electronegativity differences [7] give some rough idea of the relative heteroatom bonding components. However, stability intercomparisons are more complicated than that because *stability* is *always* relative to those of other competitive phases in each system. The latter may change from one Z element to the next, even among the binary products.

The extent of cluster condensation and the varieties of structure types among the rare-earth-metal cluster halides appear to be relatively limited by the size and number of



halides that in effect sheathe the metal clusters. A considerable gain in novelty and variety of compounds formed and in the degrees of condensation is found on change of the electronegative component from halide to, especially, telluride. This probably occurs because half as many anions are then necessary to yield roughly the same electron count per atom (\sim 2) in the metal network. Two- and three- dimensional networks are now common [8], with the separate telluride anions bound within isolated cavities, and the strength and numbers of metal-metal interactions in these appear to be less limited by "matrix" (packing) effects and more nearly intrinsic than with halides. Such effects can be judged in terms of variations of COHP values (~ overlap populations) for "bonds" versus observed distances among various metal atom pairs and the deleterious effect that neighboring telluride has on the former [5, 9, 10].

The number of R-Z systems among the tellurides is considerable, ~ 240 for the practical R and the Z listed above, and most of the novel results obtained to date [8, 10-12]have been found in relatively scattered systems rather than during systematic explorations. Moreover, negative results are seldom reported. Therefore, we have undertaken a more systematic survey of such ternary tellurides for a range of R = Sc, Y, Pr, Dy, Er-Lu and Z = Rh-Ag and Ir-Auand with a fairly regular synthetic procedure. The results soon focused on new examples of the orthorhombic $R_7 Z_2 Te_2$ structure [13, 14], although a few hexagonal R_6ZTe_2 examples (Fe₂P derivatives) [15–17] were also found. The choice of R metals reflects our earlier observations that the more unusual products appear to occur principally with Sc, Y, and the heavier lanthanides. This aspect will be discussed later in terms of some fundamental properties of the R elements.

Experimental Section

Syntheses

All materials were handled in a nitrogen or helium-filled glove box. The starting rare-earth materials were pieces of Sc, Y, Pr, Dy, Er, Tm, Yb, or Lu (Ames Lab, 99.99 % total), the Z components Ru, Rh, Pd, Ag, Os, Ir, Pt or Au as pieces or foil (Alfa, >99.5%), and Te ingots (Aldrich, 99.99 %). The syntheses started with the preparation of the corresponding RTe, for which small pieces of Rand Te in 1:1 proportions were sealed in evacuated silica tubing and heated over 16 h to 475 °C, held for 6 h, and then raised over 4 h to 850-900 °C, where they were held for 6h. Guinier X-ray powder diffraction data showed only the target phases. Mixtures of R, RTe, and Z were pelletized with a hydraulic press, and then arcmelted with a 20-30 ampere current for 20-30 s per side. The weight losses during arc-melting were < 2%. The buttons gained from arc-melting were crushed into smaller pieces, and portions ground into fine black powders for powder diffraction analyses. Our intent was to explore phase space around R₇Z₂Te₂ compositions; thus some reactions were loaded with that composition whereas some 7:2:2, and other products were also identified following exploratory reactions starting with other compositions. None of the samples showed sensitivity to moist air, at least over one day.

$R_7Z_2Te_2$ -type-Phases

All compounds were found to form during arc-melting, suggesting these were among the higher melting phases in these systems. For good quality single crystals, the crushed samples were subsequently annealed between 935 °C and 1250 °C over 4 days to 4 weeks. These were sealed into tantalum tubes, and these sealed into silica jackets for reactions run in tube furnaces below 1100 °C. Other samples in Ta containers alone were annealed above 1100 °C in a graphite-heated high vacuum furnace. The yields of the 7:2:2 compounds on annealing did, in general, not change much compared with those after arc-melting.

The targets of exploratory syntheses were of course always something new, and so many loaded compositions did not match the stoichiometry $R_7 Z_2 Te_2$. In detail, samples yielding this structure were loaded as follows: Y₇Au₂Te₂ formed in a sample with a loaded Y₁₇Au₆Te₃ composition (following Er₁₇Ru₆Te₃ [11]). Annealing at 1100 °C for seven days and cooling to 850 °C at 10 °C/h led to \sim 75 % of Y₇Au₂Te₂ plus an unknown phase, which grew to \sim 40 % at 1200 °C. A yield of 30 % Dy₇Rh₂Te₂ formed from a Dy₁₆Rh₃Te₃ composition annealed for one week at 1200 °C. Loading Dy₂₀Pd₆Te₃, Dy₅IrTe or Er₂₀Ag₆Te₃ and tempering each at four weeks at 935 °C led to 80 % Dy₇Pd₂Te₂, 20 % Dy₇Ir₂Te₂, and nearly single-phase Er7Ag2Te2, respectively. However, the last was obtained only when the sample is guenched from 1000 °C. Single crystal diffraction data were collected for Dy₇Ir₂Te₂. The Dy₇Pt₂Te₂ was obtained from samples loaded as Dy16Pt3Te3, Dy20Pt6Te3, or Dy₅PtTe that were heated to 1000 °C or 1100 °C for more than one week. The powder pattern of a Dy₅PtTe composition showed almost only Dy7Pt2Te2, whereas Er7Rh2Te2, Er7Pd2Te2 and Er7Pt2Te2 crystallized in ~90 % yields from the corresponding $Er_{12}Z_3Te_2$ samples annealed at 1250 °C for four days. The first was also gained in a 65% yield from a Er₂₀Rh₆Te₃ sample annealed at 1000 °C for 9 days, with Er₇Rh₃ as a byproduct. Furthermore, 70 % Er₇Pt₂Te₂ was obtained from an Er₁₆Pt₃Te₃ sample tempered at 1100 °C for 13 days. Er₇Ir₂Te₂ was synthesized in a 60 % yield from samples loaded as Er₁₂Ir₃Te₂ or Er₅IrTe and annealed at 1200 °C for one week. A composition of Lu₂₀Rh₆Te₃ annealed at 1000 °C for one week showed $\sim 70 \% \text{ Lu}_7 \text{Rh}_2 \text{Te}_2$.

Other Product Types

Some systems yielded only new examples of known hexagonal 6:1:2 [15] or the 17:6:3 [11] structures. Reactions with erbium and osmium gave Er_6OsTe_2 in a 80-90 % yield from $\text{Er}_{12}\text{Os}_3\text{Te}_2$ or $\text{Er}_7\text{Os}_3\text{Te}$ compositions tempered at 1250 °C for four days. More than 80 % R_6RuTe_2 was obtained from reactions loaded with $\text{R}_{20}\text{Ru}_6\text{Te}_3$, R = Dy, Er, and run at 935 °C for four weeks. The orthorhombic Er_6AgTe_2 was obtained under similar conditions. The 6:1:2 phase formed similarly from $\text{Lu}_{20}\text{Ru}_6\text{Te}_3$ or $\text{Lu}_1\text{/Ru}_6\text{Te}_3$ samples that were annealed at 1000 °C for at least one week. $\text{Lu}_{20}\text{Ru}_1\text{Ze}_3$ that was tempered at 1200 °C for one week gave 85 % of an unknown phase. However, the $\text{Dy}_{20}\text{Ru}_6\text{Te}_3$ composition annealed at 1000 °C for 9 days and quenched gave the new version of a structure known with Er [11], $\text{Dy}_{17}\text{Ru}_6\text{Te}_3$, in ~80 % yield, but an unknown product was obtained on slow cooling, without quenching.

Direct arc-melting of thulium and ytterbium test samples was not feasible because of the substantial volatility of those elements. Therefore, samples of $Tm_{10}Ru_2Te_3$ were reacted at 1125 °C for two weeks, which gave $\sim 70 \% Tm_6RuTe_2$. The same procedure with a

 Tm_5Ru_3Te composition led to TmTe and ${\sim}15\,\%$ of an unknown phase, but annealing these at 1000 °C for two weeks also led to 80 % Tm_6RuTe_2 . A sample of Tm_5Rh_3Te so yielded 20 % Tm_6RhTe_2 , 35 % of an unknown, and TmTe. The compositions $Yb_{10}Ru_2Te_3$ and Yb_5Ru_3Te reacted either at 1000 °C or at 1125 °C for two weeks exhibited little reaction except for small amounts of the 6:1:2 phase.

Some samples showed neither the 6:1:2 nor the 7:2:2 phase. These were all samples that could not be arc-melted because of high metal volatility, namely for thulium and ytterbium. $Yb_{10}Pd_2Te_3$ and Yb_5Pd_3Te compositions annealed at 1000 °C or 1125 °C for two weeks led to 40 % Yb_3Pd and 10 % Yb_5Pd_2. The powder pattern of Ho_3Pd_2 accounted for at least 30 % of the patterns from $Tm_{10}Rh_2Te_3$, $Tm_{10}Pd_2Te_3$, and Tm_5Pd_3Te samples. About 45 % of an unknown phase forms from $Tm_{10}Pd_2Te_3$ at 1125 °C. About 30 % TmAu appears when Tm_5Au_3Te is annealed at 1125 °C, but ~45 % of an unknown appears after a 1000 °C reaction. Yb-Au-Te samples show YbTe as main product and 20 % of the same unknown as from the Tm reactions. This is also true for a $Tm_{10}Au_2Te_3$ composition. The reaction temperatures used for the Tm and Yb systems were probably too high.

Four compositions in the Sc-Au-Te system, Sc₆Au₃Te, Sc₆Au₆Te, Sc₆Au₃Te₄, and Sc₁₇Au₆Te₃, all produced the same unknown phase(s) at 1100 °C. The 40 % unknown from the first does not change for the Sc₆Au₆Te composition, but vanishes at Sc₆Au₃Te₄, and increases for Sc17Au6Te3. Some of the products in the last sample decrease on reactions at 1200 °C. In addition, ScAu is found in the Sc₆Au₃Te and Sc₆Au₆Te samples, and ScTe occurs in 75 % vield for the Te-richer Sc₆Au₃Te₄. Y-Au-Te samples gave 95 % of an unknown phase from a Y₆Au₃Te sample after 1000 °C and 1100 °C reactions, but this decreased to only 25 % at 1200 °C along with 15 % of a second unknown phase. The composition Y_6Au_6Te showed 35 % of another unknown after reactions over a range of 1000 °C to 1200 °C. Finally, test experiments with the lighter lanthanide praseodymium plus nickel, ruthenium, rhodium or platinum in 7:2:2 stoichiometries gave no like targets after arc melting or subsequent annealing at 1100 °C for 12 days. Reactant PrTe was the main phase plus a presumed alloy of praseodymium and Z that showed only a systematic shift with the radii of the Z. A summary of all of these results appears later.

Powder X-ray Diffraction

Powder diffraction patterns were recorded in the 2Θ range of $5-100^{\circ}$ over 30 min with the aid of a Huber Guinier 670 imageplate diffractometer and Cu- $K_{\alpha 1}$ radiation. The samples were ground to a fine powder in the glove box and evenly distributed between two Mylar films, which were then mounted between Alrings. Diffraction data were collected immediately. Estimated yields in vol % were achieved by comparison of the observed patterns with those calculated from structures of known, neighboring compounds

Single-Crystal Diffraction Studies

Several well-formed single crystals of $Dy_7Ir_2Te_2$ were selected and protected with a layer of silicone oil. Their qualities were checked with a single-crystal X-ray diffractometer (Stoe Image Plate Diffraction System, IPDS II) and a complete intensity data set was collected at ambient temperature with the aid of graphite-monochromatized Mo- K_{α} radiation. Data reduction and a numerical absorption correction according to crystal shape optimization were applied utilizing the STOE program package. The WinGX suite of programs [18], including SHELXS-97 and SHELXL-97 [19], were employed for structure solution and refinement. The last refinement cycles included atomic positions and anisotropic displacement parameters for all atoms. Some data collection and refinement parameters for Dy₇Ir₂Te₂ are listed in Table 1. Further details of the crystal structure of Dy₇Ir₂Te₂ are available from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CDS-420220, the names of the authors, and the citation of the paper, E-mail: crysdata@fiz-karlsruhe.

Table 1. Some X-ray data collection and refinement parameters for $Dy_7Ir_2Te_2$.

Empirical formula	$Dy_7Ir_2Te_2$
Formula weight $/g \cdot mol^{-1}$	1777.10
Crystal system	orthorhombic
Space group, Z	Imm2 (No. 44), 2
a /Å	3.9552(8)
b /Å	15.645(3)
c /Å	9.392(2)
$V/Å^3$	581.2(2)
$d_{\rm calcd.}/{\rm g}\cdot{\rm cm}^{-3}$	10.155
Absorp. coeff. (Mo- K_{α}) μ /mm ⁻¹	72.033
Θ range /deg.	2.53-29.04
F(000)	1440
Range in <i>h k l</i>	$-5 \le h \le 5, -17 \le k \le 21,$
	$-12 \le l \le 12$
Reflections collected	2972
Independent reflections	905 ($R_{\rm int} = 0.0692$)
Data /parameters	905 /38
Goodness-of-fit on F^2	1.140
Final R_1 , wR_2 indices	
$[I > 2\sigma(I)]$	0.0416, 0.0905
(all data)	0.0476, 0.0920
Largest diff. peak and hole $/e \cdot Å^{-3}$	4.734, -3.382

Results and Discussion

These explorations of ternary rare-earth-metal-rich telluride systems have led to a good variety of new compounds, as identified mainly with the aid of powder patterns calculated for known R-Z-Te structure types. These results give better insights into the breadth of possible phases. The most general new feature is the common but not uniform occurrence of orthorhombic R_7Z_2 Te₂-type phases. Heretofore, only a few examples [13, 14] were known, namely, $Er_7Ni_2Te_2$ and $Lu_7Z_2Te_2$, Z = Ni, Pd, Ru, in contrast to the seemingly more common orthorhombic and hexagonal R_6 ZTe₂-type compounds. However, the present study has turned up 10 more R_7Z_2 Te₂ examples, Y with Au, Dy with Pd, Ir or Pt, five more for Er with Z = Rh, Pd, Ag, Ir, or Pt, and Lu with Rh. These are inevitably evident in the powder patterns obtained directly after arc-melting, indicating their appreciable thermal stabilities as well. Unit cell data for the new members of this family are listed in Table 2.

Table 2. New compounds with the orthorhombic $\text{Er}_7\text{Ni}_2\text{Te}_2$ -type structure (*Imm2*).

Compound	<i>a</i> /Å	b /Å	c /Å	Volume /Å ³	Lines indexed
$\overline{Y_7Au_2Te_2^{a)}}$	4.041(2)	15.53(3)	9.687(9)	607.9(1)	13
$Dy_7Pd_2Te_2^{a}$	3.935(2)	15.541(1)	9.541(6)	588.8(7)	4
$Dy_7Ir_2Te_2^{b}$	3.9552(8)	15.645(3)	9.392(2)	581.2(2)	
$Dy_7Pt_2Te_2^{a}$	3.9569(5)	15.607(3)	9.539(2)	589.1(1)	10
$Er_7Rh_2Te_2^{a}$	3.8877(7)	15.50(1)	9.363(3)	564.1(3)	8
$\mathrm{Er}_{7}\mathrm{Pd}_{2}\mathrm{Te}_{2}^{\mathrm{a}}$	3.9166(6)	15.452(7)	9.513(2)	575.7(2)	8
$\mathrm{Er}_{7}\mathrm{Ag}_{2}\mathrm{Te}_{2}^{\mathrm{b}}$	3.949(6)	15.676(2)	9.409(2)	582.4 (4)	
$\mathrm{Er}_{7}\mathrm{Ir}_{2}\mathrm{Te}_{2}^{\mathrm{a})}$	3.9399(7)	15.435(3)	9.328(3)	567.3(1)	13
Er ₇ Pt ₂ Te ₂ ^{a)}	3.9301(9)	15.458(9)	9.476(3)	575.6(3)	11
$Lu_7Rh_2Te_2{}^{a)}$	3.854(1)	15.290(5)	9.289(4)	547.4(2)	16

a) Lattice constants refined from Guinier powder data. b) Lattice constants refined from IPDS-II single crystal data.

Table 3 summarizes seven other new examples found among the eight R and the eight Z (Ru, Rh, Pd, Ag, Os, Ir, Pt, Au) combinations studied that are isostructural with other known ternary compositions, as well as 14 instances in which new patterns could not be assigned. (only negative results are omitted.) The number of unknown structures with gold in the last group is appealing. All of the Z members tested except Os acted as interstitials frequently. The Rdependences generally followed the observations that in part prompted this study (below). An exception might be that Dy, Er and Lu are more frequent participants than Tm or Yb although the last two have been less well studied. However, comparisons when both Z and R are varied are not that simple. Major complications in such homologous series may arise from irregular changes in the competitive phases that define stability. Thus, series of comparative R-Z binary phases often exhibit irregular variations in composition and structure with changes in Z. The electron counts may also be important although these last two effects have not been studied. Finally, the four experiments with Pr (above) were undertaken to test the proposition that the light lanthanides were uncommon, even unknown, participants in this ternary telluride chemistry, and the negative results appear to reaffirm that postulate.



Figure 1. Off-[100] projection of the orthorhombic $Dy_7Ir_2Te_2$ structure along the short *a* axis.

Structural Description

A slightly-off-[100] section of the structure of Dv₇Ir₂Te₂ is shown in Figure 1. The principal building units outlined consist of distorted, Ir-centered, tricapped trigonal prisms of Dy that share basal trigonal faces to form columns along the *a* axis. Adjacent columns along *c* are displaced along the projection axis by a/2 by means of a simply and common regularity. As depicted in Figure 2, the interconnections into puckered layers in this direction take place via bifunctional Dy1 and Dy3 that are members of a trigonal prism in one column and also cap a rectangular face in its neighbor. This type of function is common in many metalrich structures, often showing staggered bridging in three directions via tri-capped trigonal prisms, but this structure features only the bicapped motifs here. Finally, the threedimensional structure is generated by Dy4 atoms that facecap on adjoining layers along the b direction, Figure 1. In

Table 3. Additional literature and experimental results for ternary R-Z-Te phases^{a),b)}.

	Sc	Y	Pr	Dy	Er	Tm	Yb	Lu
ternary tellurides	$Sc_{5}Ni_{2}Te_{2} [20], Sc_{6}ZTe_{2} (H) (Z = Mn, Fe, Co, Ni, Ru, Os, Rh, Pd, Ir, Ag, Cu, Cd) [15, 17], Sc_{14}Z_{3}Te_{8} (Z = Ru, Os) [21]$	$\begin{array}{l} Y_5 Z_2 T e_2 \\ (Z = F e, C o, \\ N i) \left[22, 23 \right], \\ Y_6 Z T e_2 \left(O \right) \\ (Z = R h, P d, \\ A g, Y) \left[22 \right] \end{array}$		Dy_6ZTe_2 (H), (Z = Fe-Ni) [16], Dy_6RuTe_2 (H), Dy ₁₇ Ru ₆ Te ₃	$\begin{array}{l} E_{r_4}ZTe_2,\\ (Z=Co, Ni),\\ E_{r_3}Z_2Te_2\\ (Z=Co, Ni) \left[24\right],\\ E_{r_6}ZTe_2 \left(H\right)\\ (Z=Co, Ni, Ru)\\ \left[10\right], Er_6AgTe_2 \left(O\right),\\ Er_6OsTe_2 \left(H\right)\\ Er_7Ni_2Te_2 \left[11\right],\\ Er_{17}Ru_6Te_3 \left[12\right],\\ Er_{21}Ir_8Te_4 \left[13\right]\end{array}$	Tm ₆ RuTe ₂ (H), Tm ₆ RhTe ₂ (H)		Lu ₆ RuTe ₂ (H), Lu ₆ AgTe ₂ (O) [10], Lu ₇ Z ₂ Te ₂ (Z = Ni, Pd, Ru) [14]
unknown tellurides	Au	Au (3 phases)		Ru, Ir	Pd	Ru, Rh, Pd, Au	Rh, Au	Ru

a) All known compounds are listed in italics with the corresponding references. All new $R_7Z_2Te_2$ type phases are listed only in Table 3. b) H and O distinguish between hexagonal ($P\bar{6}2m$, No. 189) and orthorhombic R_6ZTe_2 phases (*Pnma*, No. 62), respectively.

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addition, Te1 is surrounded by a bicapped trigonal prism of Dy, and Te2, by a monocapped trigonal prism of Dy, common ways of accommodating the separate anions.



Figure 2. ~ [010]-view of a portion of the chains of condensed trigonal prismatic dysprosium atoms (black), each centered by an iridium atom (smaller spheres), that lie along c (Figure 1) in Dy₇Ir₂Te₂. Note that prismatic Dy1 and Dy3 atoms in one column constitute the face-capping atoms in its neighbours.

Appreciable distortions accompany the formation of this structure type with its reduced symmetry and stoichiometry change. The simplest measures are the Dy-Ir distances, which range over only 2.84 to 2.91 Å within the trigonal prisms, but these increase to 3.10 and 3.80 Å for the facecapping dysprosium atoms. The different functionalities of, and the nearest neighbors to, the four types of dysprosium atoms are reflected in much larger and more diverse variations among Dy-Dy distances. In more regular cases, prismatic-prismatic atom distances are usually somewhat smaller than for prismatic-face-capping separations, depending somewhat on the relative height of the trigonal prisms (along c here). In $Dy_7Ir_2Te_2$, the Dy1 and Dy3 atoms play both prismatic and face-capping roles (Figure 1, Figure 2), and show d(Dy-Dy) ranges of 3.47–3.81 Å around Dy1 and a contrasting 3.47-3.69 Å about Dy3. The former is the same as a 3.47-3.81 Å range about Dy2, even though this has only a prismatic role in the structure, whereas an intermediate 3.64-3.77 Å is found around Dy4, which is only face-capping between chains. However, the numbers of Te bound to each type of R atom is also known to have a substantial effect on its R-R distances (and bond populations) [9, 20]. Thus appreciable (polar) covalent Dy-Te bonding naturally raises the higher lying 5d (and other) levels on Dy and leads to weaker Dy-Dy interactions with its less affected neighbors. Figure 1 shows that Dy3 is indeed more shielded from Te than the others, with only one Te neighbour versus two (Dy1) or three (Dy2, Dy4) for the others. (Dy3 also has one more Ir neighbour.) This is presumably the reason that Dy3 has about a 0.13 Å smaller value for its upper limit of bond lengths to its like

neighbours even though it also plays both prismatic and capping roles in the structure. Finally the relatively large size of Te is what fixes both the short *a* axis at 3.995 Å, and the prismatic heights as well, Figure 2. These fixed separations for all atoms have been omitted from the d(Dy-Dy) considerations above.

Distinctions Among Rare-Earth Elements in Ternary Metalrich Tellurides

Tellurides of the sort described here exhibit some remarkable differences among the rare-earth elements in their metal-richest phases, namely, that substantially all examples occur with scandium, yttrium, and at least the heavier lanthanide members that have been better studied, dysprosium through lutetium. Extensive earlier investigations among the condensed cluster halides of the rare-earth elements that were likewise stabilized by diverse centered transition metals (e.g., $R_{12}(Z)X_{14}$) also revealed a few similar but less extreme differences wherein unusual distortions occurred for particular combinations of R and Z. (Recall that the degrees of cluster condensation are less in the anion-richer halides, and the metal-metal interactions are correspondingly less numerous.) Thus, certain cluster chain structure types show significant distortions, Y₃I₃Ir but not Pr₃I₃Ru, for example [26]. Other distortions are found among the tetrameric $R_{16}Z_4I_{20}$ oligomers and their differentiation from the chain structure of the isomeric R_4ZI_5 is similarly related [27]. In all cases, the distortions appear to lead to more and shorter R-R, R-Z and Z-Z distances. Köckerling and Martin [28] produced an attractive interpretation of all of these distortions in terms of those R and Z that had the more similar orbital energies and thence better mixing between the (mainly) valence d orbitals on R and Z. They compared the last effects in terms of the differences in first ionization energies of the respective R and Z elements. Orbital energies tabulated for EHTB calculations work similarly [26, 27].

The tellurides appear to exhibit more extreme versions of these differences, presumably because of the greater degrees of condensation and thence increased numbers of contacts among R and Z. Moreover, certain R elements evidently form no such materials, and the stable condensed metalrich tellurides are heavily concentrated among Sc, Y and (so far) Dy through Lu. (However, it would appear that Gd and Yb have not been well investigated with respect to the latter region.) Since there was a concern that our R sampling had not been very uniform (you fish in places that yield fish!), four additional reactions were run under the standard protocol with $Pr_7Z_2Te_2$ compositions, but nothing pertinent was seen (text in Experimental Section; Table 3).

An extension of the above ideas regarding unusual distortions observed in the analogous condensed cluster halides qualitatively fits changes in telluride stabilities as well, and more broadly. Figure 3 shows on the left a plot of the I1 + I2 energies [29] for the rare-earth elements with energies increasing downward. These are considered to afford some



Figure 3. Left: The variation of the sum of the first and the second ionization energies within the lanthanide series of elements and those for three typical transition metals below (dashed lines). Elements below the thick black line generally form ternary rare-earth-metal-rich tellurides. Right: Representations of variation of the degrees of orbital mixing that accompany different relative energies of R and Z orbitals.

readily available measures of the relative orbital energy levels (and atom electronegativities) for R. Also marked below are the analogous values for three fairly extreme Zmembers: Mn, Rh and Pt. The panel on the right reminds us that, in the simplest picture, the magnitudes of bonding/ mixing of orbitals on different atoms vary inversely with the energy difference between their valence (nd) orbitals (all other things being equal). We take this parallel between the ionization energy properties of R and Z to reflect by some crude measure the observation that the R-Z interactions, and thence bond energies and relative stabilities follow the differences in rare-earth orbital energies as measured by ionization parameters fairly well. Of course, there are many other features that enter into bond strengths and phase stabilities (and always with respect to those of the most stable decomposition products), but this simple measure gives a striking parallel. Again, the relative properties and stabilities of the Gd and Tb analogues have not been studied well, although it is noteworthy that only Sc, Gd and Dy have so far yielded the unusual binary Sc₂Te-type structure [30].

Clearly the results presented herein are nowhere near the final answers. Some of the more attractive problems are a clearer positioning of Gd and Tb in these systems and, especially, the many unidentified and doubtlessly novel telluride products implied by the unknown phases listed in Table 3.

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