This article is published as part of the Dalton Transactions themed issue entitled:

Synthetic Solid State Chemistry

Guest Editor Duncan Gregory University of Glasgow, UK

Published in issue 26, 2010 of Dalton Transactions



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Novel condensation of Au-centered trigonal prisms in rare-earth-metal-rich tellurides: $Er_7Au_2Te_2$ and $Lu_7Au_2Te_2$ [†]

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Received 11th January 2010, Accepted 27th April 2010 First published as an Advance Article on the web 12th May 2010 DOI: 10.1039/c000650p

A new monoclinic structure occurs for Er₇Au₂Te₂ according to X-ray diffraction analysis of single crystals grown at 1200 °C: C2/m, Z = 4, a = 17.8310(9) Å, b = 3.9819(5) Å, c = 16.9089(9) Å, $\beta =$ $104.361(4)^{\circ}$. The isostructural Lu₇Au₇Te₂ also exists according to X-ray powder pattern means, a =17.536(4) Å, b = 3.9719(4) Å, c = 16.695(2) Å, $\beta = 104.33(1)^{\circ}$. The structure contains zigzag chains of condensed, Au-centered tricapped trigonal prisms (TCTP) of Er along c that also share basal faces along b to generate puckered sheets. Further bi-face-capping Er atoms between these generate the three dimensional network along a, with tellurium in cavities outlined by augmented trigonal prismatic Er polyhedra. Bonding analysis via LMTO-DFT methods reveal very significant Er-Au bonding interactions, as quantified by their energy-weighted Hamilton overlap populations (-ICOHP), ~49% of the total for all interactions. These and similar Er-Te contributions sharply contrast with the small Er-Er population, only ~14% of the total in spite of the high proportion of Er-Er contacts. The strong polar bonding of Er to the electronegative Au and Te leaves Er relatively oxidized, with many of its 5d states falling above the Fermi level and empty. The contradiction with customary representations of structures that highlight rare-earth metal clusters is manifest. The large Er-Au Hamilton overlap population is in accord with the strong bonding between early and late transition metals first noted by Brewer in 1973. The relationship of this structure to the more distorted orthorhombic (Imm2) structure type of neighboring Dy₇Ir₂Te₂ is considered.

Introduction

An impressive number of new structures and bonding novelties have been discovered in the rare-earth-metal-rich telluride systems.¹ This direction evolved from the rather spectacular results for similarly electron-poor cluster halides of the rare-earth metals R (group 3 and lanthanides). Seemingly regular cluster/network electronic requirements for R bonding in both families necessitate the inclusion of substantially electron-richer interstitial atoms (Z) within all R cages.^{2,3} However, the particular stability of R clusters centered by the late transition metals in the halide and telluride "salts" has been qualitatively attributed to the strength of the polar heteroatomic bonding between early and late (electron-poor and electron-rich) transition metals (Tn) first put forth by Brewer and Wengert.⁴ This concept has led to the discovery of a large number of new phases and structures stabilized by 3d, 4d, and 5d transition metal interstitials.^{1,5,6} Interestingly, the more productive R members appear to be Sc, Y and the heavier lanthanides, particularly Gd, Dy, Er and Lu (to date), a differentiation has been attributed to the fact that the more tightly bound valence orbitals in this group are closer in energy to those of the usual Z.⁷⁻⁹ A more diverse structural chemistry arises for the ternary tellurides relative to the halides because only about half as many of the monoanions are now necessary to achieve about the same electron count per network metal atom (~2). This leads to notably greater degrees of cluster condensation of the tellurides and to more complex, two- or three-dimensional network structures.^{1,10,11} A unifying feature in these and other recently reported metal-rich ternary tellurides is a common structural motif: tricapped trigonal prisms (TCTP) of the rare-earth metal centered by a late transition metal as well as similar basic coordination of Te by R.^{9,11}

Gold incorporation has recently been found to stabilize an appreciable group of novel structures and stoichiometries among a remarkable variety of related electron-deficient Zintl phase relatives¹²⁻¹⁵ (polyanionic salts of active metals, counterparts of the foregoing cationic polymetal salts¹⁶). This has given us good incentive to examine Au reactions with the poly-rare-earth-metal salts as well. The distinctive behavior of gold in the former phases evidently originates with prominent relativistic effects¹⁷ that particularly stabilize (and contract) its 6s orbital, reduce the atom's effective radius, and therewith bring 5d states back into a prominent bonding role. Another expression of these effects is that they markedly increase the Mulliken electronegativity of gold (5.77 eV), putting it in the neighborhood of Te and Se.¹⁸

Earlier extended-Hückel examinations of the bonding among the halide examples have generally suggested the presence of strong R–Z and somewhat weaker R–R bonding.¹⁹⁻²² However, the various Mulliken overlap population (COOP) values are not directly comparable, and no more quantitative studies have yet appeared. However, LMTO-type first-principle calculations for

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[†] Electronic supplementary information (ESI) available: Displacement ellipsoid parameters, distances and individual –ICOHP data, and other structural views. CSD reference number 420862. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000650p

several novel gold-stabilized Zintl-phase derivatives^{14,15,23,24} have greatly illuminated new and more quantitative aspects of their bonding in terms of (Hamilton) bond populations. The better representation of gold's 5d orbitals leads to distinctively enhanced bonding relative to those of the following, largely p-bonded components. The present article reports the first results among the R-based halides and tellurides for (1) gold substitution in a new structure type for $Er_7Au_2Te_2$ (and $Lu_7Au_2Te_2$) and (2) such *ab* initio calculations as aids to understanding and representing the bonding. Only one analogous reduced halide system is known with gold, the fairly unremarkable cubic La_3AuI_3 (Ca₃PI₃ type) in which gold centers condensed, nominal La6 octahedra condensed into a spiral network.²⁵ In contrast to the present results, the polytypic orthorhombic Er₇Ni₂Te₂ structure type (Imm2)²⁶ occurs for several of the heavier R and a fairly large number of other transition metal interstitials: R(Z) = Dy (Pd, Ir, Pt), Er (Rh, Ir, Ni, Pd, Pt),9 and Lu (Ni, Ru, Rh, Pd).11 The Y7Au2Te2 composition also exists in the orthorhombic structure rather than that of the new Er₇Au₂Te₂.9

Experimental

Syntheses

All reactants and products were handled in nitrogen- or argonfilled glove boxes with less than 0.4 ppm H₂O levels. The general techniques were as before.^{5,7,9-11} The starting materials were Ho, Er, Tm, Yb, Lu (Ames Laboratory, 99.95% total), Au (Ames Laboratory, 99.95%), and Te pieces (Aldrich, 99.999% metal basis). Crystals of Er₇Au₂Te₂ were first obtained during an exploratory investigation of rare-earth metal-rich phase space in the Er-Au-Te system. Mixtures of Er, Au and the preformed AuTe₂ (>95%, from reaction of the elements in a SiO₂ container at 800 °C for 12 h) were arc-melted in various proportions and then annealed. One such reaction designed to test the existence of an orthorhombic Er₇Ni₂Te₂ type analogue⁹ revealed the existence of the new phase along with ErTe (NaCl type) (significant Er evaporation also occurred during the arc-melting process). A better approach, which presumably also expedited homogenization during arcmelting, employed preformed ErAu and ErTe, as synthesized in ~95% yields from reactions of the elements as above. These and Er metal in 2:2:4 molar proportions were cold pressed into a pellet and arc-melted at \leq 30 amp for about 30 s within an Arfilled glove box. Homogenization was improved by flipping the pellet and repeating the process twice. This product contained ~80% of the new orthorhombic phase, as later judged by the single crystal result, plus AuTe₂. Single crystals of this Er₇Au₂Te₂ were obtained by annealing the product in a sealed Ta tube at 1200 °C for one week in a graphite-heated vacuum furnace (Labmaster Thermal Technology Inc. 1000-2560-FP20) at $< \sim 10^{-6}$ torr. This shiny black phase turns dull within 24 h on standing in moist air at room temperature.

Similar reactions of Ho gave only HoTe and Ho₂Au, whereas extreme metal vaporization made analogous reactions with Tm and Yb unproductive. However, the isostructural Lu₇Au₂Te₂ was obtained in >80% yield from that composition, a = 17.536(4), b = 3.9719(4), c = 16.695(2) Å, $\beta = 104.33(1)^{\circ}$. More metalrich compositions yielded Lu₂Au (Co₂Si-type)²⁷ as the major product.

Powder diffraction

X-Ray powder patterns were secured at ambient temperature with the aid of a Huber 670 Guinier (image-plate) camera and Cu-K α radiation ($\lambda = 1.540598$ Å). Phase distributions on a volume basis were estimated from the powder patterns of products relative to those calculated according to single crystal refinements. Lattice constants were obtained from least-squares refinements of measured and indexed powder reflections from the stoichiometric as-cast samples using the WinXPOW program.²⁸

Semiquantitative microprobe analyses (EDS) of the $Er_7Au_2Te_2$ single crystal used for X-ray diffraction and of several others were performed with a JEOL 5910LV scanning electron microscope equipped with a Noran-Vantage energy-dispersive spectrometer. The average composition from various spots on four different crystals, normalized with respect to Au, was $Er_{6.94(2)}Au_2Te_{1.94(1)}$, in good agreement with the single crystal X-ray refinement result.

Structure determination

Dark, irregular, and metallic-looking crystals were separated from the crushed product of the reaction composition $\text{Er}_8\text{Au}_2\text{Te}_2$ and were mounted in glass capillaries inside the glove box. A total of 5031 reflections (3 sets of 606 frames with exposure times of 10 s per frame) covering $2.48^{\circ} \le 2\theta \le 56.44^{\circ}$ were collected at room temperature with the aid of a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromatized Mo-K α radiation ($\lambda = 0.71069$ Å). Unit cell parameters were determined from 990 reflections indexed on a C-centered monoclinic basis. Intensity data were integrated and corrected for Lorentz, polarization and (empirical) absorption effects with the aid of SAINT²⁹ and the SADABS subprograms,³⁰ respectively. The empirical absorption corrections proved to be adequate in spite of the relatively high absorption coefficient, 79.9 mm⁻¹. During the final refinement, 1560 unique reflections [R(int) = 6.31%] were used.

The structure solution was obtained by direct methods and refined by full-matrix least-squares method on F_0^2 with the aid of SHELXTL v 6.1.³¹ The centrosymmetric space group C2/m was selected for refinement according to systematic absence conditions and intensity statistics ($|E^2 - 1| = 0.897$). No systematic absence violations or inconsistent equivalents were observed. A symmetry check by PLATON indicated that no crystallographic symmetry was missing. One out of 13 peaks calculated by direct methods was immediately rejected on the basis of distance, and the other 12 peaks were initially assigned as Er. Convergence was achieved at a residual of ~9%. Isotropic displacement parameters for two positions were too small and two others were too large, clearly indicating the probable positions of the Au and Te. A few more refinement cycles on that basis led to a relatively featureless Fourier map and to reasonable displacement parameters and interatomic distances. Further anisotropic refinement led to well behaved ellipsoids for all peak positions and $R_1 = 4.59\%$, w $R_2 = 9.38\%$ $(I > 2\sigma(I))$ at convergence. The largest peaks in the final Fourier difference map (3.98 and $-3.50 \text{ e} \text{ Å}^{-3}$) were 1.1 and 1.3 Å from erbium atoms.

Some crystallographic and refinement data for the structure are listed in Table 1. The corresponding atomic coordinates, standardized with STRUCTURE TIDY,³² and the

Table 1	Selected cryst	al and refinement	t parameters for	$Er_7Au_2Te_2$
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Empirical formula	$\mathrm{Er}_{7}\mathrm{Au}_{2}\mathrm{Te}_{2}$
Crystal system	Monoclinic
Space group, Z	C2/m, 4
a/Å	17.8310(9)
b/Å	3.9819(5)
c/Å	16.9089(9)
$\beta/^{\circ}$	104.361(4)
Volume/Å ³	1163.1(5)
$ ho_{\rm cal}/{ m g~cm^{-3}}$	10.394
μ/mm^{-1}	55.337
Index ranges	$-23 \le h \le 23$
	$-5 \le k \le 5$
	$-22 \le l \le 22$
Reflections collected	5031
Independent reflections	1560 [R(int) = 0.0631]
Data/parameters	1560/70
Goodness-of-fit on F^2	1.061
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0459$
	$wR_2 = 0.0938$
R indices (all data)	$R_1 = 0.0636$
	$wR_2 = 0.1016$
Largest diff. peak and hole/e $Å^{-3}$	3.976, -3.505

isotropic-equivalent displacement parameters are listed in Table 2. More refinement data and anisotropic displacement parameters are provided in the ESI.[†]

Band calculations

The electronic band structure and densities-of-states for Er₇Au₂Te₂ were calculated self-consistently by the tight-binding, linear muffin-tin orbital (TB-LMTO) method33-35 within the atomic spheres approximation (ASA) with the Stuttgart code.³⁶ Exchange and correlation were treated in a local spin density approximation,37 and scalar relativistic effects were taken into account.³⁸ In ASA, space is filled with overlapping Wigner-Seitz (WS) spheres at each atomic site. An automated procedure is used to optimize the WS sphere radii, requiring that the overlapping potential be the best possible approximation to the full potential within the limit of 16% overlap between any atomcentered spheres.³⁹ The WS radii so determined were: erbium 1.72-1.82 Å; gold 1.59-1.60 Å; and tellurium 1.73-1.77 Å. For space filling, 18 empty spheres (ES) with WS radii of 0.64-1.20 Å were also introduced. The basis set included Er 6s/(6p)/5d, Au 6s/6p/5d/(5f), Te 5s/5p/(5d)/(4f), and a 1s function for the empty spheres (downfolded orbitals^{40,41} in parentheses); the Er 4f orbitals were treated as filled core orbitals. Reciprocal space integrations to determine self-consistent charge densities, and densities-of-states (DOS) curves were performed by the tetrahedron method⁴² on grids of 282 *k*-points in the irreducible wedges of the corresponding Brillouin zones. For bonding analysis, the energy contributions of all electronic states for selected atom pairs were calculated as a function of energy according to the crystal orbital Hamilton population (COHP) method.⁴³ The (average) energy-weighted sums of these up to E_F give –ICOHP values for the individual pair-wise overlap populations. The Fermi levels are all set to zero, and the –COHP data are plotted with respect to energy as negative values correspond to bonding interactions.

Results and discussion

Syntheses

A new monoclinic $Er_7Au_2Te_2$ was discovered during exploration of metal-rich phase space in the Er-Au–Te system by methods very similar to those used earlier for other R–Tn–Te systems.⁹⁻¹¹ Arc-melting a pellet pressed from suitable proportions of ErTe, ErAu, and Er gave distinctively higher yields than from AuTe₂ and Er because of the significant vapor pressure of liquid $Er.^{44}$ Attempted extensions to Ho, Tm, Yb, Lu proved fruitful only as far as the isostructural $Lu_7Au_2Te_2$ (Experimental), the Tm and Yb systems probably being irregular because of the high vapor pressures of the metals as well as the same fundamentals that lead to their formation of dihalides. The formation of Au compounds only with Er or Lu for these tellurides is special inasmuch as orthorhombic $R_7Tn_2Te_2$ types are known instead for 14 examples of the heavier Dy, Er, Tm, Lu with late transition metals (groups 8 to 10, Cu, Ag) as well as $Y_7Au_2Te_2$.^{9,11} These are compared later.

Structure description

Fig. 1 shows a projection of the new monoclinic $\text{Er}_7\text{Au}_2\text{Te}_2$ structure along the short *b* axis (3.9819(5) Å). A simplistic view of the structure is gained by outlining all Er–Er separations between the shortest, 3.45 Å, and 3.98 Å, the *b* axis repeat length. This rather conventional representation helps illuminate the connectivities within the major building blocks in the structure, but it doesn't recognize stronger interactions elsewhere, as discussed later. The

Table 2Atomic coordinates and isotropic-equivalent displacement parameters ($Å^2 \times 10^3$) for $Er_7Au_2Te_2$

Atom Er1	Wyckoff site, sym.		x	у	Z	U(eq) ^a
	4i	т	0.00160(8)	0	0.33363(8)	12(1)
Er2	4i	m	0.17552(8)	0	0.53172(8)	13(1)
Er3	4i	m	0.19106(8)	0	0.31896(8)	13(1)
Er4	4i	m	0.33787(8)	0	0.01995(8)	13(1)
Er5	4i	m	0.57520(8)	0	0.17146(9)	14(1)
Er6	4i	m	0.78097(8)	0	0.19451(8)	11(1)
Er7	2d	2/m	0	1/2	1/2	14(1)
Er8	2a	2/m	0	0	0	13(1)
Aul	4i	т	0.17180(7)	0	0.11081(7)	13(1)
Au2	4i	т	0.38046(7)	0	0.60085(7)	14(1)
Te1	4i	m	0.0648(1)	0	0.8496(1)	12(1)
Te2	4i	т	0.3668(1)	0	0.3376(1)	11(1)

^a U(eq) is defined as one-third of the trace of the orthogonalized Uij tensor.



Fig. 1 ~[010] section of the monoclinic $\text{Er}_7 \text{Au}_2 \text{Te}_2$ structure (*C2/m*): Er, red; Te, olive, brown; Au, yellow, orange. All atoms lie on mirror planes at y = 0, 1/2. Puckered sheets defined by zigzag chains of condensed Au-centered TCTPs of Er are highlighted by black bonds and overlaid golden lines. Note the bifunctional face-capping Er7 and Er8 atoms on inversion centers.

Er₇Au₂Te₂ is built primarily from the distorted, Au-centered, tricapped trigonal prisms (TCTP) of Er, the same building units as in the orthorhombic Er₇Ni₂Te₂-type structure. These TCTPs share basal trigonal faces to generate metal-columns along the view direction (b), whereas contiguous columns arrayed roughly along *a* are alternately displaced along the projection axis by b/2and condensed by sharing functions. This rather common mode produces sheets of condensed TCTP layers via bi-functional Er2, Er3, Er4 and Er5 atoms that are both members of trigonal prisms in one column and capping atoms on the rectangular side faces of trigonal prisms in adjacent columns. (The side view is given in ESI.[†]) However, what are slightly puckered sheets of TCTP in the higher symmetry orthorhombic $Dy_7Ir_2Te_2$ appear here as $4 \times$ 2 zigzag chains of TCTP, as marked by an overlaid golden line in Fig. 1. The effects of this new mode appear in the distinctive TCTP environments about Au1 (yellow) and Au2 (orange), with the three shortest Er-Er distances (7-1-3-5) and a greater range of d(Er-Er)) in the TCTP about Au2 (3.45–3.96 Å) than around Au1 (3.59–3.92 Å). The zigzag puckered layers are further joined into a three dimensional structure along a via bi-face-capping Er8 and Er7 atoms that lie on inversion centers at x = 1/2, a functionality that is also present in the Er₇Ni₂Te₂ family. Finally, these puckered metal layers are also held together by distant pairs of Te1 and Te2 spaced likewise along b, with a distorted monocapped trigonal prism of Er around Te1 and a more regular bicapped trigonal prismatic environment about Te2. Although formal Te²⁻ anions within such condensed poly-metal networks (and the halides in their family of analogues) have often been concluded to just be large spacers, *ab initio* calculations make clear this is not correct, below. Note that representations or indications of Er-Au and Er-Te bonding are as usual not marked in Fig. 1, although these turn out to be of major importance.

Theoretical considerations

These results lead to bonding concepts that differ substantially from those implied by usual pictorial description of this structure (Fig. 1). The calculated total densities-of-states (DOS), their atomic and orbital breakdowns (partial DOS), and the pair-wise –COHP populations by bond type according to LMTO–ASA calculations for $\text{Er}_7\text{Au}_2\text{Te}_2$ are presented in Fig. 2 as a function of energy. (A low lying band at –13.0 to –11.0 eV (not shown) is largely core-like and nearly all Te s in origin.) Not surprisingly, a substantial DOS at the Fermi level (dashed line) is indicative of a metallic property. Major contributions here arise from Er d \gg p > s and lesser Au d states, as seen from the atom-resolved PDOS in Fig. 2(b) and 2(c). Overall, the relatively well-separated band components in DOS and PDOS align well with the COHP functions, allowing fairly ready assignment of all other features in Fig. 2. (Note that the ordinate scales change downward in this.)



Fig. 2 Densities-of-states (DOS) (a), partial DOS by atom and orbital types (b–d), and crystal orbital Hamilton populations (–COHP, eV per bond-mol) (e) for monoclinic $Er_7Au_2Te_2$. The dashed line marks the Fermi energy (E_F). Note the ordinate scale expansion downward.

The lowest –COHP feature around –6 eV originates with roughly equal numbers of Er 5d, 6s, and 6p states mixed with the dominant Au 5d and 6s, Fig. 2(b) and 2(c). Its smaller width parallels the higher binding energy. The COHP band around –4 eV arises principally from Er (d,s,p) and Te 6p states but with significant Au d,s contributions in the lower regions as well. The width of the Te p band clearly denies the presence of simple Te^{2–} anionic states. And the bands in DOS around –2 and –1 eV,

Atom pair	-ICOHP (avg. per bond)	No. of bonds per cell	-ICOHP (cumulative, per cell)	% contribution	
Er–Er	0.174	104	17.10	14.0	
Er–Au	0.846	72	60.91	48.9	
Er–Te	0.699	66	46.13	37.1	

Table 3 Individual (average) and cumulative –ICOHP components (eV/bond mol) in $Er_7Au_2Te_2$, Z = 4

Fig. 2(a), both originate with Au, principally 6p, and Er 5d but with appreciable contributions of Te1 p as well in the lower of the two bands. (Site-differentiated PDOS for gold show no significant differences between Au1 and Au2, and the same applies to Er7 and Er8 relative to the rest.) Thus the bands around -4 and -2 eV as well as around E_F all feature substantial contributions from all three elements and more delocalized bonding. The same is reflected by the 9 to 13 nearest neighbors for each Er as well as the nine around Au.

Significant charge transfer among all three elements can be recognized too. Nearly all the Te 5p states as well as the Er-Te COHP function fall below $E_{\rm F}$ (Fig. 2(d,e)). Likewise, a negative oxidation state for gold can be readily inferred inasmuch as many Au 6s and 6p and almost all Au 5d states lie below $E_{\rm F}$, in contrast to its classical 6s¹ valence configuration. In other words, the orbital distributions of Er, Fig. 2(b), clearly reflect a substantial oxidation of the element. Note that many of the Er 6s and 6p states now lie below -2 eV, whereas a large and increasing number of its 5d orbitals have been raised in energy, many to above $E_{\rm F}$ (COHP, Fig. 2(e)). Thus the more penetrating 6s and 6p orbitals fall in energy faster as the metal is oxidized. The above Er-Au dispositions are in fact general and characteristic of bonding between pairs of early and late d elements in binary phases that likewise behave as "polar intermetallics", e.g., Ti-Fe and Ti-Ru.45 This same characteristic for analogous halides of rare-earth-metal clusters stabilized by late transition metals^{2,5} can be qualitatively recognized in earlier extended-Hückel (EHTB) outputs for these, noting that this empirical method does a poor job of modeling virtual R states above $E_{\rm F}$ and that the valence d bands are often too narrow.19

Finally, the energy-weighted sums of the COHP bond data, – ICOHP (total Hamilton (overlap) populations) provide a much better analysis of relative bond populations or indices and hence approximate bond strengths, as summarized in Table 3. The average –ICOHP value per contact (bond·mol) of each type are listed in column 2. The structure itself exhibits fixed intrinsic relationships between the number of each bond type (interacting atom pairs) per cell, and the products of these and individual – ICOHP values yield some good measures of the different pair-wise contributions to the overall population (stability), column 4. The percentage distributions by bond type in the last column furnish plausible assessments of the relative weights of the separate bond types in the phase.

The results are quite striking: distinctively larger –ICOHP values per bond are associated with the polar bonds Er–Au and Er–Te, whereas the homoatomic bonding among the majority, but electron-depleted, Er atoms (Fig. 2(b)) is quite small. (There are no significant Au–Au or Te–Te contacts in the structure.) Even the preponderance of Er–Er interactions, 49% of the total of all types, does not overcome their small individual contributions. Thus Er–Er makes up only 14% of the total –ICOHP value, whereas Er–

Au comprises nearly 50%, certainly enhanced by the substantial relativistic effects for Au.¹⁵ The common and convenient way of representing such structures in terms of the network defined by a major element, as for 64% Er in Fig. 1, is certainly misleading regarding the bonding. Similar effects of polar bonding are found for many electron-poor and metallic Zintl-phase relatives.^{12–15,24,25}

R₇Tn₂Te₂ structural comparisons

Results of our recent and fairly systematic synthetic explorations among metal-rich ternary tellurides of the late 4d and 5d transition metals and the heavier R elements have appreciably expanded (to 14) the collection of alternative orthorhombic $Er_7Ni_2Te_2$ -type compounds.^{9,11} It is noteworthy that among these, $Y_7Au_2Te_2$ and four close neighbors, $R_7Tn_2Te_2$ for R = Dy, Er and Tn = Ir, Pt, appear to adopt only the orthorhombic structure, not the new monoclinic version of Er₇Au₂Te₂ and Lu₇Au₂Te₂. Reasons for the structural change between the more common Imm2 Er₂Ni₂Te₂ structure type for the neighboring $Dy_7Ir_2Te_2$ (the only one with refined structural data) and the new $C2/m \operatorname{Er}_7\operatorname{Au}_2\operatorname{Te}_2$, are apt to be manifold and complex. However, comparisons of some of the multiple features between these two are quite helpful and definitive, namely, that the smaller, higher symmetry orthorhombic structure exhibits distinctly more distorted interconnections between the TCTP sheets but no evidence that fundamental atom size differences are important (their molar volumes are not significantly different).

A relatively small decrease in metallic radius is expected from Dy to Er, only of the order of 0.02 Å. Although some radius scales among the 5d metals show an increase of ~0.08 Å from Ir to Au,⁴⁶ our experiences with the more anionic states of these in intermetallic phases containing early active metals indicate that a size *decrease* of the same magnitude (~0.08 Å) occurs between Ir and Au as the relativistic effects increase.⁴⁷ (It is also clear that the Pt radius is ~0.08 Å greater than that of Au in isotypic BaTnIn₃ phases, Tn = Pt, Au, with BaAl₄-type structures.⁴⁸)

The new structure type with 12 independent atom sites and two types each of Au and Te (Z = 4) is less distorted on average than the orthorhombic Dy₇Ir₂Te₂ (Z = 2) with seven independent atoms and one type of TCTP. Differences in particularly the ranges of d(R-R) and d(R-Z) in the TCTP arrays are somewhat greater for the single TCTP type in Dy₇Ir₂Te₂, but the distances alone are not very different in the two. But it is particularly the intersheet R-R bridge bonds between the novel bi-face-capping (b.f.c.) Er7 and Er8 and the Er trigonal prisms in adjacent sheets (Fig. 1) (and the angles therewith) that are distinctly more symmetric in the lower symmetry monoclinic structure than in Dy₇Ir₂Te₂. In other words, relaxations around the two independent *bridging* R (as well as, implicitly, among larger numbers of the Tn and Te) atoms in Er₇Au₂Te₂ allow the bridged TCTP array to pack/bond more efficiently. The bridging Er7 and Er8 lie on inversion centers within Published on 12 May 2010. Downloaded by University of Illinois at Chicago on 28/10/2014 18:30:34

rectangular prisms defined by Er in the adjoining slabs so the *trans*bonding Er4–Er8–Er5 angles are 180°, Fig. 1. The fairly regular packing in this structure also give Er7 and Er8 two additional Au2 or Au1 neighbors (at 3.17 and 3.04 Å) in the adjoining slabs, respectively; in a reverse sense, these are also the closest facecapping Er atoms about both TCTP around Au, by 0.3 and 0.5 Å, respectively.

On the other hand, the arrangement in higher symmetry and smaller orthorhombic $Dy_7Ir_2Te_2$ is a good deal less regular, both in the packing within the TCTP-based sheets and around the interbridging, face-capping Dy4 (pictured in Fig. S2, ESI†). The *trans*-bridging-angles Dy1–Dy4–Dy3 are now 158°, not 180°, and the opposed rectangular faces of the distorted rectangular Dy prism about Dy4 now have a dihedral angle of 17.1° between them. Furthermore, the centering Ir atoms beyond those faces are 0.6 Å or more further away than in the title phase, and the other face-capping Ir–Dy distances about the Dy trigonal prisms are also larger. Only the innermost features of the common R_6 Tn prisms are similar in the two compounds, the Dy–Ir values being ~0.02 Å larger.

We lack enough detail to ferret out the countervailing factors that preclude this transformation from occurring in all cases. The stronger bonding of the smaller gold may be particularly important, but higher symmetry and smaller structures are often favored when sensitive band features are not present around $E_{\rm F}$.

Conclusions

Strong polar Er–Au bonding arising in part from substantial relativistic effects for Au together with major Er–Te interactions appear in a new monoclinic network structure for $(\text{Er},\text{Lu})_7\text{Au}_2\text{Te}_2$. On the other hand, the large number of Er–Er contacts still makes the smallest contributions to the overall Hamilton bond populations. The new structure exhibits apparently more nearly ideal packing of condensed Er(Au) tricapped trigonal prisms than the more common orthorhombic Er₇Ni₂Te₂-type polytype. High coordination numbers and extensive delocalized bonding are characteristic of the more polar electron-poor intermetallic phases.

Acknowledgements

The guidance and insights of G. J. Miller are gratefully acknowledged. This research has been supported by the National Science Foundation, Solid State Chemistry, *via* Grants DMR-0444657 and -0853732 and was performed in the Ames Laboratory of the U.S. Department of Energy.

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