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Ternary Rare Earth Osmium Aluminides $R_{7+x}Os_{12}Al_{61+y}$ Belonging to a Structural Family with Layered Topology

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The 10 intermetallic compounds $R_{7+x}Os_{12}Al_{61+y}$ (R = Y, Nd, Sm, Gd–Tm) were prepared by arc-melting of the elemental components. They crystallize with a hexagonal structure very similar to that of $Y_{7.28}Re_{12}Al_{61.38}$. The structure was determined from four-circle diffractometer data of $Y_{7+x}Os_{12}Al_{61+y}$: $P6_3/mcm$, $a = 1301.5(2)$ pm, $c = 903.0(2)$ pm, $Z = 1$. Four atomic sites, all located on the 6_3 axis, show fractional occupancy, resulting in the composition $Y_{7.86(1)}Os_{12}Al_{61.51(4)}$, corresponding to the Pearson symbol *hP*90–8.63. The structure may be viewed as consisting of alternating atomic layers of two kinds, although chemical bonding within and between the layers is of similar character as can be judged from the near-neighbor environments, where all of the 11 atomic sites have high coordination numbers. One kind of layers (A) is relatively loosely packed and contains the yttrium and some aluminum atoms. The other kind (B) consists of the osmium and the remaining aluminum atoms in a nearly hexagonal close-packed arrangement. These layers are stacked in the sequence ABAB. A similar building principle has recently been recognized for several other structures of ternary intermetallic compounds of rare earth and transition metals with a high content of aluminum or gallium, where the structures of $CeOsGa_4$, $Ho_3Ru_4Ga_{15}$, and $Y_2Pt_6Al_{15}$ are the most recent examples. This structural family is briefly reviewed. The cell volume of $Yb_{7+x}Os_{12}Al_{61+y}$ indicates a mixed or intermediate valence character +2/+3 for the ytterbium atoms of this compound.

Introduction

In recent years, a large number of ternary intermetallics of rare earths R and transition metals T with a high content of a main group metal M (mostly aluminum or gallium) have been synthesized, e.g., the series $R_2T_3M_9$ with T = Rh, Ir,[1] RT_2Al_{20} and $R_6T_4Al_{43}$ with T = early transition metals,[2a] $R_2Ru_3Ga_{10}$ and RRu_2Ga_8,[2b] $Ce_4Ni_6Al_{23}$,[3] $CePdGa_6$,[4] $Gd_{1.33}Pt_3(Al, Si)_8$, and $Gd_{0.67}Pt_2(Al, Si)_5$,[5a] RAu_3Al_7,[5b] $R_3T_4Al_{12}$ with T = Ru, Os,[6] $R_3Ru_4Ga_{15}$,[7] $R_3T_{2+x}Al_{9-x}$ with T = Cu, Ag,[8] and $R_2Pt_6Al_{15}$.[9] Interesting physical properties of such compounds are observed when the rare earth component is cerium, europium, or ytterbium, in which cases the mixed valence, the heavy fermion behavior, and the magnetic order together with the electrical and thermal properties are investigated.[1–4] Metallurgists may find such aluminum-rich intermetallics to improve the mechanical properties of aluminum alloys.[10] Here, our interest lies mainly in the structural chemistry of such compounds.

With osmium as the transition metal component, only a few compounds of similar compositions have been reported. $Sc_6Os_7Al_{16}$ with an ordered cubic Th_6Mn_{23} type structure has been known for some time.[11] We have recently characterized the series $R_3Os_4Al_{12}$ with the $Gd_3Ru_4Al_{12}$ type structure.[6] The

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Table 1. Lattice Constants of Ternary Rare Earth Osmium Aluminides with the $Y_{7+x}Re_{12}Al_{61+y}$ Type Structure[a]

compound	*a* (pm)	*c* (pm)	*V* (nm^3)
$Y_{7+x}Os_{12}Al_{61+y}$	1300.8(2)	902.6(1)	1.3228
$Nd_{7+x}Os_{12}Al_{61+y}$	1308.7(2)	908.4(1)	1.3473
$Sm_{7+x}Os_{12}Al_{61+y}$	1305.8(2)	906.3(1)	1.3383
$Gd_{7+x}Os_{12}Al_{61+y}$	1302.5(2)	904.3(1)	1.3286
$Tb_{7+x}Os_{12}Al_{61+y}$	1301.9(2)	903.4(1)	1.3260
$Dy_{7+x}Os_{12}Al_{61+y}$	1299.2(2)	902.3(1)	1.3189
$Ho_{7+x}Os_{12}Al_{61+y}$	1298.4(2)	901.5(1)	1.3162
$Er_{7+x}Os_{12}Al_{61+y}$	1297.6(2)	901.4(1)	1.3145
$Tm_{7+x}Os_{12}Al_{61+y}$	1297.3(2)	900.3(1)	1.3122
$Yb_{7+x}Os_{12}Al_{61+y}$	1299.6(2)	902.4(1)	1.3198

[a] Standard deviations in the place values of the last listed digits are given in parentheses throughout the paper.

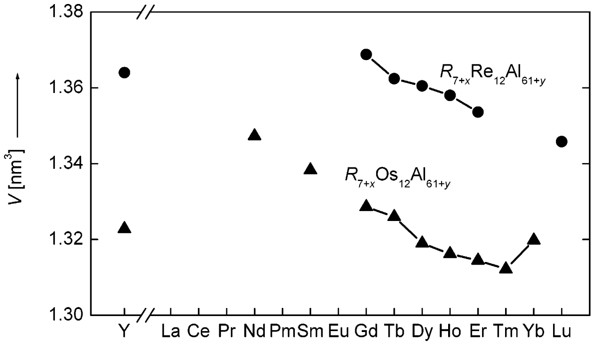

Figure 1. Cell volumes of the new osmium containing aluminides with $Y_{7+x}Re_{12}Al_{61+y}$ type structure as compared to the cell volumes of previously reported[14,15] nearly isotypic rhenium compounds.

Table 2. Crystal Data for $Y_{7+x}Os_{12}Al_{61+y}$

space group	*P*6$_3$/*mcm* (No. 193)
a (pm)	1301.5(2)
c (pm)	903.0(2)
V (nm^3)	1.3247
Z	1
T (°C)	21
λ (pm)	71.07
composition	$Y_{7.86(1)}Os_{12}Al_{61.51(4)}$
Pearson code	*hP*90−8.63
formula mass	4641
ρ_{calcd} (g/cm^3)	5.82
μ (cm^{-1})	382
R (*F*)[a]	0.033
R_w (F^2)[a]	0.151

[a] $R = \sum|F_o - |F_c||/\sum F_o$; $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0547 \cdot P)^2 + 340.65 \cdot P]$, where $P = (\max(F_o^2) + 2F_c^2)/3$.

compounds ROs_2Al_{10} (R = La, Pr, Nd) have a much higher aluminum content (with the atomic ratio R/Os/Al = 8:15:77) and crystallize with the $YbFe_2Al_{10}$ type structure.[12] The aluminides reported here have a similar composition (10:15:75) as the latter series. They are formed with the smaller rare earth elements including neodymium which also forms the $YbFe_2Al_{10}$ type compound.

Experimental Section

Sample Preparation and Lattice Constants. The samples were prepared from the elemental components by arc-melting. The rare earth elements (nominal purities ≥99.9%) were purchased in the form of ingots which were cut to pieces prior to the cold-pressing. Osmium (≥99.9%) and aluminum (Fluka, >99%) were purchased as powders. The three components were mixed in the atomic ratio 1:2:12, pressed into pellets of approximately 150 mg, and arc-melted under purified argon from both sides. The resulting buttons were crushed and treated in diluted hydrochloric acid to remove minor amounts of some (unknown) impurities.

Compact pieces of the ternary aluminides have silvery metallic luster. The powders are black and stable in air for long periods of time. Energy-dispersive X-ray fluorescence analyses in a scanning electron microscope did not reveal any impurity elements heavier than sodium.

The samples were further characterized with the Guinier technique using monochromated Cu Kα_1 radiation and α-quartz (a = 491.30 pm, c = 540.46 pm) as an internal standard. To facilitate the assignment of indices to the resulting powder patterns, we calculated theoretical patterns[13] using the positional parameters of the structure resulting from the single-crystal investigation. The lattice constants (Table 1) were obtained by least-squares fits. The cell volumes of the new osmium compounds are plotted in Figure 1 together with those of previously reported[14,15] rhenium compounds which have a very similar, albeit not entirely isotypic, crystal structure.

Structure Determination. A single crystal of the yttrium compound was selected for the structure determination on the basis of Laue diffractograms. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation, $\theta/2\theta$ scans, a scintillation counter with pulse-height discrimination, and background counts at both ends of each scan. An empirical absorption correction was applied to the data on the basis of ψ scans. The crystal data are listed in Table 2 and in more detail in a table of the Supporting Information.

The structure was solved and refined with the program package SHELX-97.[16] For the full-matrix least-squares refinements, atomic scattering factors were used, corrected for anomalous dispersion as provided by the program. The weighting scheme reflected the counting statistics, and an isotropic parameter correcting for secondary extinction was optimized as a least-squares variable.

To check for the proper assignment of the atomic positions, we refined occupancy parameters together with variable displacement parameters and a fixed scale factor. No serious deviations from the ideal occupancies were found for most atomic positions, where the occupancy parameters varied between 97.9(4)% for the Y1 positions and 105.8(9)% for the Al5 position. These occupancy parameters were fixed at 100% during the final least-squares cycles. Exceptions were all atomic positions situated on the 6_3 axis, where during the final least-squares cycles the occupancy parameters of two yttrium (Y2 and Y3) and two aluminum (Al6 and Al7) positions were refined. The displacement parameters of these atoms could not be varied. They were fixed to the average isotropic displacement parameters of the corresponding atoms with full occupancy. The highest 20 peaks in the final difference Fourier synthesis were all very close to fully occupied atomic positions, and therefore, they were not suited for additional atomic sites. The results of this

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Table 3. Atomic Parameters of $Y_{7.86(1)}Os_{12}Al_{61.51(4)}$[a]

atom	$P6_3/mcm$	occupancy	x	y	z	B_{eq}
Y1	6g	1	0.39191(4)	0	$^1/_4$	0.63(1)
Y2	4e	0.099(2)	0	0	0.2143(5)	0.63*
Y3	2a	0.731(3)	0	0	$^1/_4$	0.63*
Os	12i	1	0.20279(1)	2x	0	0.45(1)
Al1	12k	1	0.20120(9)	0	0.0288(1)	0.89(2)
Al2	12k	1	0.61584(9)	0	0.1036(1)	0.87(2)
Al3	12j	1	0.16524(8)	0.28417(9)	$^1/_4$	0.53(2)
Al4	12j	1	0.2703(2)	0.52548(9)	$^1/_4$	0.99(3)
Al5	12i	1	0.58992(5)	2x	0	0.48(1)
Al6	4e	0.125(5)	0	0	0.087(2)	0.73*
Al7	2b	0.506(8)	0	0	0	0.73*

[a] The last column contains the equivalent isotropic B values (in units of 10^4 pm^2), with the exception of those marked with an asterisk which were held constant.

refinement, including the interatomic distances, are summarized in Tables 2−4 and in two tables of the Supporting Information.

Discussion

The 10 new isotypic rare earth osmium aluminides are represented by their cell volumes in Figure 1 together with the corresponding nearly isotypic rhenium compounds reported earlier.[14,15] Generally, these cell volumes follow a smooth function. The upturn for $Yb_{7+x}Os_{12}Al_{61+y}$ indicates a mixed or intermediate +2/+3 valence of the ytterbium atoms in this compound. For a purely divalent state, the cell volume of this compound would be much greater.

The crystal structure of the rhenium compounds has been determined first for $Y_{7.28(2)}Re_{12}Al_{61.38(3)}$ and $Ho_{7.32(1)}Re_{12}Al_{61.48(4)}$,[14] and subsequently also for $Gd_{7.23(1)}Re_{12}Al_{61.70(4)}$, $Dy_{7.50(2)}Re_{12}Al_{61.17(4)}$, and $Lu_{7.61(1)}Re_{12}Al_{61.02(4)}$.[15] The somewhat variable composition of these compounds is due only to the fractional occupancy of the rare earth and aluminum sites at the 6-fold axis. It correlates with the atomic size of the rare earth elements,[15] and we expect a similar dependence of the composition on the size of the rare earth atoms also for the corresponding osmium compounds, reported here. The structure of the presently determined osmium compound $Y_{7.86(1)}Os_{12}Al_{61.51(4)}$ differs from that of the rhenium compounds in that three crystallographic sites were found at the 6-fold axis for the rhenium compounds and four sites for the osmium compound. The fourth atomic site in $Y_{7.86(1)}Os_{12}Al_{61.51(4)}$ is the Al7 position at 2b, 0, 0, 0, with an occupancy of 50.6(8)%. The neighboring 4e site, 0, 0, 0.086(2), in the osmium compound has an occupancy of only 12.5(5)%. In the rhenium compounds. the occupancy of the 4e site varies between 43(1)% for $Gd_{7.23(1)}Re_{12}Al_{61.70(4)}$ and 25(1)% for $Lu_{7.61(1)}Re_{12}Al_{61.02(4)}$. The assignment of rare earth and aluminum atoms and the order for the occupied sites on the 6-fold axis was discussed at some length for the rhenium compounds. The same assignments were assumed for the present refinement of the osmium compound. A total of 3.37 atoms (1.86 Y + 1.51 Al) need to be assigned to one translation period of 903 pm; i.e., the average shortest distance between two atoms on the 6-fold axis is rather short with 268.0 pm. However, one has to consider that most of these atoms have lower coordination numbers than the atoms at the fully occupied sites, and therefore, shorter interatomic distances are to be expected.

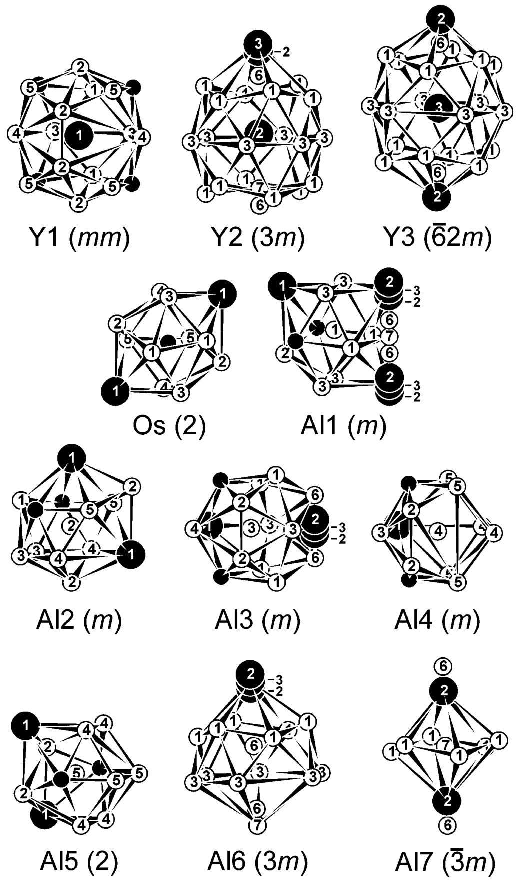

Figure 2. Coordination polyhedra in the structure of $Y_{7+x}Os_{12}Al_{61+y}$. The site symmetries of the central atoms are indicated in parentheses. The positions of the Y2, Y3, Al6, and Al7 atoms, all situated on the 6_3 axis, have fractional occupancy. This affects their coordination polyhedra as well as the polyhedra of the neighboring Al1 and Al3 atoms. In all of these affected coordination polyhedra, the hexagonal axes extend in the vertical direction.

The yttrium atoms Y1, Y2, and Y3 in $Y_{7.86(1)}Os_{12}Al_{61.51(4)}$ occupy three crystallographic sites with occupancies of 100%, 9.9(0.2)%, and 73.1(0.3)%, respectively. These large atoms have high coordination numbers (CN) with 18 (Y1) and 20 (Y2 and Y3) neighbors, respectively. The coordination polyhedra are shown in Figure 2. It can be seen that the Y2 and Y3 atoms have 18 aluminum neighbors. In addition, they have a total of two additional neighbors at sites with fractional occupancy (Y2, Y3, Al6, Al7) capping hexagons formed by the Al1 atoms.

The osmium atoms have 10 aluminum neighbors forming a pentagonal antiprism which is capped by two yttrium atoms (CN = 12). The average Os−Al distance amounts to 263.9 pm, considerably shorter than the sum of the CN = 12 ("metallic") radii of 278.4 pm (r_{Os} = 135.2 pm, r_{Al} = 143.2 pm, as computed from the data given for the elemental structures in Donohue's monograph[17]). This indicates strong Os−Al bonding.

All of the five aluminum sites with full occupancy (Al1−Al5) have two osmium neighbors, between 7 and 10 aluminum neighbors, and between 1 and 3 yttrium neighbors. The total CNs vary somewhat, not only from one central

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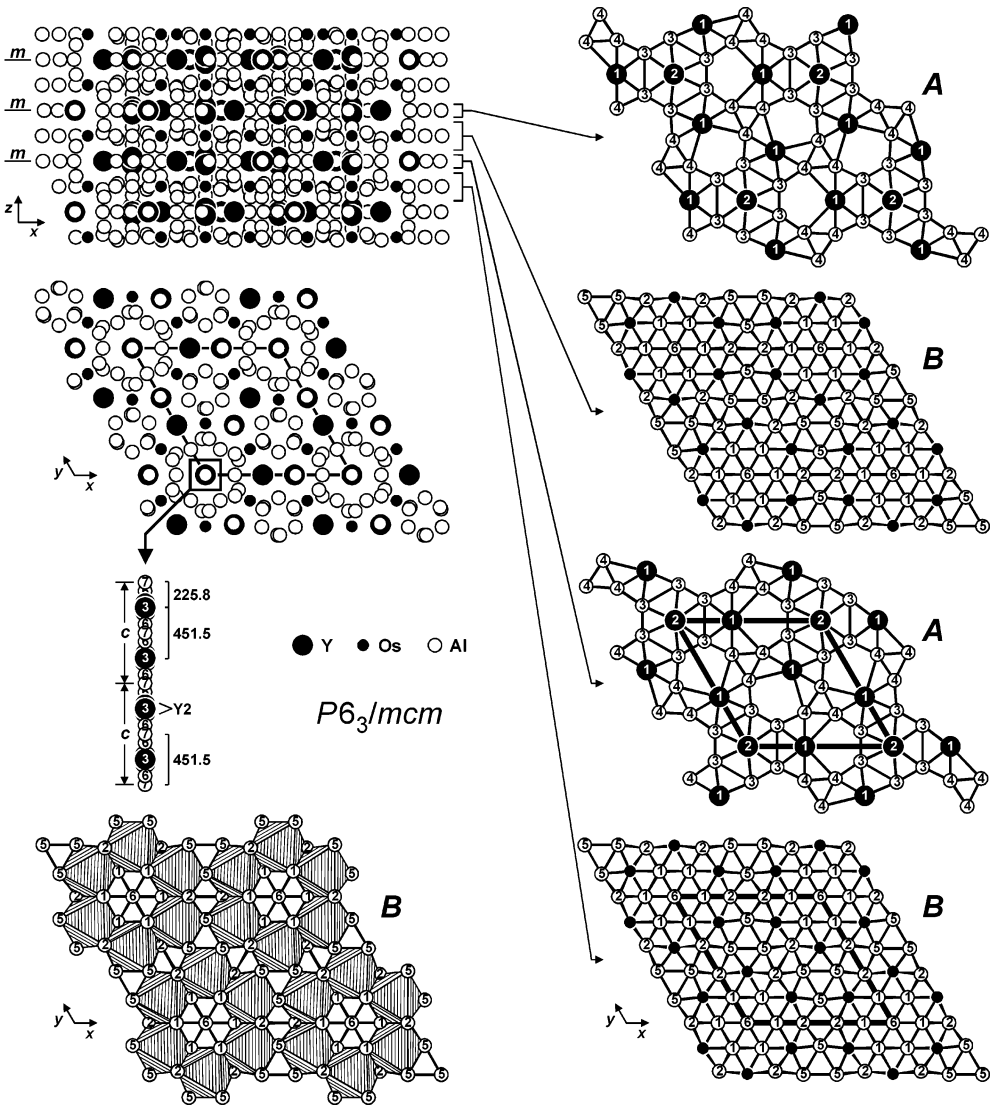

Figure 3. $Y_{7.28}Re_{12}Al_{61.38}$ type crystal structure of $Y_{7+x}Os_{12}Al_{61+y}$. All atoms of this structure are shown in projections perpendicular and parallel to the hexagonal axis in the upper left-hand part of the figure. Two kinds of atomic layers (A, B) can be discerned extending perpendicular to this axis. They are shown on the right-hand side. Layers of type A coincide with mirror planes. They contain all yttrium and some aluminum atoms. Layers of type B contain all osmium and the remaining aluminum atoms. They are puckered in such a way that the aluminum atoms form octahedra around the osmium atoms. These octahedra are distorted and strongly compressed along the hexagonal *c* axis of the structure. They share corners and edges as is shown in the lower left-hand side of the structure. Also shown is the sequence of the atomic sites of the Y2, Y3, Al6, and Al7 atoms with fractional occupancy located on the 6-fold axis. Of these interpenetrating atoms, only the outer Y2 and Al6 atoms are shown in the A and B layers.

aluminum atom to the other, but also because neighbors with the large Al2−Al2 and Al3−Al3 distances of 354.9 and 372.5 pm may be counted as neighbors or not. Another variable results from the fractional occupancy of the Y2, Y3, Al6, and Al7 positions (Figure 2). Thus, the total CNs for these five aluminum sites amount to between 12 and 14. At short distances, these aluminum atoms have between 7 and 9 aluminum neighbors with a weighted average of 281.2 pm, slightly shorter than the Al−Al distance of 286.3 pm in elemental aluminum (fcc, CN = 12), thus indicating considerable Al−Al bonding, as could be expected for a compound with such a high content of aluminum. The sites of the Al6 and Al7 atoms have occupancies of only 12.5(0.5)% and 50.6(0.8)%, respectively. The Al6 site has 12 aluminum neighbors at fully occupied positions, plus a total of one yttrium and one aluminum neighbors positioned at several sites with fractional occupancy. The Al7 atoms have a rather small CN with only six Al1 and two more neighbors (Y2, Al6) above and below, on sites with fractional occupancy. Thus, in view of the small CN of the Al7 atoms, the rather short Al7−Y2 distance of 258.0 pm can be rationalized.

It has been commented by one reviewer that in view of the small coordination number of the Al7 site this position might actually be occupied by oxygen atoms. In considering this possibility, one has to keep in mind that this site is quite close to the two Al6 sites above and below with an Al6−Al6 distance of only 157 pm. Thus, only one of these three positions (1Al7 + 2Al6) can be occupied at the same time. The total occupancy of these three sites with aluminum atoms is 75.8% [0.506(8) + (2 × 0.125(5))]. We have refined the occupancy parameters for these sites assuming (again) fixed displacement parameters of 0.73×10^4 pm^2 and using the scattering factor of oxygen. This resulted in a total occupancy of 136.2(∼2.0)%. Assuming (for another least-squares

Table 4. Interatomic Distances in the Structure of $Y_{7.86(1)}Os_{12}Al_{61.51(4)}$[a]

Y1:	2Al4	304.7	Al1:	1Al7	263.2	Al4:	2Os	263.3
	2Al3	310.0		2Os	266.3		1Al3	272.7
	2Al1	318.6		1Al2	266.5		2Al5	275.4
	2Al2	319.5		2Al1	267.0		2Al4	276.2
	2Al2	320.0		1Al6	267.0		2Al5	285.9
	4Al5	334.4		2Al3	273.1		1Y1	304.7
	4Os	341.0		1Al6	281.9		2Al2	317.0
Y2:	(1Y3	32.3)		2Al3	286.9	Al5:	2Os	256.2
	(1Y2	64.5)		1Y2	310.8		2Al2	269.4
	(1Al6	115.2)		1Y1	318.6		2Al4	275.4
	(1Al6	179.7)		1Y3	329.3		2Al4	285.9
	(1Al7	193.5)		1Y2	341.7		2Al5	299.7
	1Al7	258.0		1Y2	349.9		2Y1	334.4
	1Al6	271.8		1Y3	363.3	Al6:	(1Al7	78.3)
	3Al1	310.8		1Y2	386.3		(1Y2	115.2)
	6Al3	323.3	Al2:	1Al2	264.3		(1Y3	147.5)
	1Al6	336.3		1Al1	266.5		(1Al6	156.6)
	3Al1	341.7		2Os	268.0		(1Y2	179.7)
	3Al1	349.9		2Al5	269.4		3Al1	267.0
	3Al1	386.3		2Al3	280.2		1Y2	271.8
	1Y2	387.0		2Al4	317.0		3Al1	281.9
	1Y3	419.2		1Y1	319.5		1Al6	294.9
Y3:	(2Y2	32.3)		1Y1	320.0		1Y3	304.0
	(2Al6	147.5)		1Al2	354.9		1Y2	336.3
	(2Al7	225.8)	Al3:	2Os	265.7		6Al3	353.9
	2Al6	304.0		1Al3	268.1		1Al7	373.2
	6Al3	321.7		1Al4	272.7	Al7:	(2Al6	78.3)
	6Al1	329.3		2Al1	273.1		(2Y2	193.5)
	6Al1	363.3		2Al2	280.2		(2Y3	225.8)
	2Y2	419.2		2Al1	286.9		2Y2	258.0
Os:	2Al5	256.2		1Y1	310.0		6Al1	263.2
	2Al4	263.3		1Y3	321.7		2Al6	373.2
	2Al3	265.7		2Y2	323.3			
	2Al1	266.3		2Al6	353.9			
	2Al2	268.0		1Al3	372.5			
	2Y1	341.0						

[a] These distances were calculated with the lattice constants as determined from the single-crystal data. All distances smaller than 390 pm are listed. In addition, some greater distances are listed between atomic sites located at the 6_3 axis. Such distances may also be rather short but do not need to occur because they extend between sites with fractional occupancy; in that case, they are listed in parentheses. The standard deviations are all equal to or smaller than 0.2 pm with the exception of distances involving sites with fractional occupancy, where they may be as large as 1.4 pm (Y2−Al6, Al6−Al7) and 2.7 pm (Al6−Al6).

refinement) that the Al6 sites are occupied by aluminum atoms, and oxygen is positioned only at the Al7 site, the total occupancy of the three adjacent sites is lowered to 121.6(∼2.0)% [1.014(16) + (2 × 0.101(5))]. Thus, we consider it as very unlikely that the Al7 site is occupied solely by oxygen atoms. On the other hand, *some* oxygen may be present at this site. Nevertheless, from its local environment with a CN of 8, it is certainly not a typical oxygen site. A mixed occupancy of one atomic site by two elements of very different character, however, is not very appealing. Also, one should keep in mind that this site with the Wyckoff designation 2*b* accounts for only 2.2% of all atomic sites of the structure. Even if it were occupied to (say) 50% by oxygen atoms, corresponding to the formula $Y_{7.86}Os_{12}Al_{60,50}O$, this would amount to an oxygen content of only 0.35 wt %. It would be very difficult to prove such a low oxygen content or to exclude it during the synthesis. Finally, we have refined this structure also assuming the Al7 site to be occupied by osmium atoms. Considering the interatomic distances, this is an attractive alternative, although the CN is low. This refinement (with the displacement parameter fixed at 0.56×10^4 pm^2) led to an occupancy of 6.6(1.3)%, corresponding to the formula $Y_{7.86(1)}Os_{12.13(1)}Al_{60.52(3)}$ as compared to the formula $Y_{7.86(1)}Os_{12}Al_{61.51(4)}$ assuming the Al7 site to be occupied only by aluminum atoms. The difference in the composition is small, and we preferred the latter formula, last not least for simplicity.

In the earlier publications on the rhenium containing $Y_{7.28}Re_{12}Al_{61.38}$ type compounds,[14,15] the overall architecture of the structure has not been discussed. We have now recognized that this structure may be viewed as belonging to a family of layered structures with a common building principle. This is shown in Figure 3 with the structure of $Y_{7+x}Os_{12}Al_{61+y}$ as a new example. In the upper left-hand corner of that figure, the structure is shown in two projections perpendicular and parallel to the 6-fold axis. Two kinds of atomic layers can be visualized, both extending perpendicular to the hexagonal axis. They are designated with the letters A and B and are shown at the right-hand side of the figure. The layers of the type A contain all yttrium atoms (of the interpenetrating Y2 and Y3 atoms, only the Y2 position is shown) and some of the aluminum atoms. These layers are situated on mirror planes, and therefore, with the exception of the slightly displaced Y2 positions, these layers are completely flat. These layers consist of a tessellation of mostly triangles, but also pentagons, and therefore, these layers are less densely packed than the layers of type B. These latter layers form a hexagonal close-packed arrangement. They contain all osmium and the remaining aluminum atoms (again, of the interpenetrating Al6 and Al7 atoms, only the outer Al6 atoms are shown). These layers are somewhat puckered in such a way that the osmium atoms obtain six aluminum neighbors within the plane, forming a strongly compressed and distorted Al_6 octahedron (this octahedron consists of the Al1, Al2, and Al5 atoms; the four other aluminum neighbors of the osmium atoms, the Al3 and Al4 atoms, belong to the adjacent layers A above and below). The compressed Al_6 octahedra within the B layers share edges and corners, as is shown at the lower left-hand side of Figure 3.

One unit mesh (the two-dimensional unit cell) of layer A has the composition $Y_4Al_{12} = 4YAl_3$ (counting the partially occupied Y2 and Y3 sites with a total occupancy of 92.9% as one site). The layers B have a mesh content of Os_6Al_{19} (again counting the Al6 and Al7 positions with a total occupancy of 75.8% as one site). The layers A and B are stacked in the sequence ABAB along the *c* direction, resulting in an overall content for the three-dimensional cell of $(2 \times 4YAl_3) + (2 \times Os_6Al_{19})$ yielding the formula $Y_8Os_{12}Al_{62}$ for the ideal composition.

This building principle for several structures of intermetallic compounds with a high content of the main group elements M has been recognized only recently for several (mainly) aluminides and gallides.[6,7] All of these structures contain layers of the type A and B. However, it must be emphasized that this is only a topological principle. Mechanically, the compounds show no preferred cleavage. In that way, they resemble the close-packed structure of the elements with AB stacking for the hexagonal close-packed structure, or ABC stacking for the cubic close-packed structure. Another, less well-known, family of intermetallics with topologically layered character is the family of tetra-

Table 5. Layered Topology of Some Intermetallics $R_xT_yM_z$ with a High Content of the M Component[a]

structure type $R_xT_yM_z$	ratio $(x\mathrm{R} + y\mathrm{T})/z\mathrm{M}$	space group	Z	stacking sequence	literature
$Gd_3Ru_4Al_{12}$	0.5833	$P6_3/mmc$	2	ABAB	6, 21
$Y_2Co_3Ga_9$	0.5556	$Cmcm$	4	ABAB	22, 23
$Er_4Pt_9Al_{24}$	0.5417	$P\bar{1}$	1	ABBAB	23
$Sc_{1.2}Fe_4Si_{9.8}$[b]	0.5306	$P6_3/mmc$	1	ABBABB	9, 24
$CeOsGa_4$	0.5	$Pmma$	6	ABAB	25
$Ho_3Ru_4Ga_{15}$	0.4667	$Pnma$	4	ABAB	7
$Y_{7.28}Re_{12}Al_{61.38}$	0.3141	$P6_3/mcm$	1	ABAB	14, this work
$CaCr_2Al_{10}$	0.3	$P4/nmm$	4	ABAB	26, 27
$YbFe_2Al_{10}$	0.3	$Cmcm$	4	ABAB	27−29
$DyRe_2Al_{10}$[c]	0.3	$P\bar{1}$	5	ABABABABAB	30, 31
$TbRe_2Al_{10}$[d]	0.3	$Cmcm$	8	ABABABAB	27
$LuRe_2Al_{10}$[d]	0.3	$Cmcm$	12	ABABABABABAB	29, 30

[a] The unit mesh contents R_xM_n and T_yM_m ($n + m = z$) of the various layers A and B, respectively, are shown in Figure 4. [b] The structure of $Sc_{1.2}Fe_4Si_{9.8}$ has been refined in space group $P6_3/mmc$ with $Z = 1$.[24] This is the subcell. For an ordered superstructure, the ideal composition is $Sc_2Fe_6Al_{15}$ with $Z = 2$, as has been demonstrated for the structures of $Ce_2Pt_6Ga_{15}$,[32] $Gd_2Pt_6Al_{15}$,[5a] and $Y_2Pt_6Al_{15}$.[9] [c] The structure of $DyRe_2Al_{10}$ has been refined in space group $P\bar{1}$. The true symmetry is probably higher.[31] [d] For the structures of $TbRe_2Al_{10}$ and $LuRe_2Al_{10}$, there are two ways of distinguishing layers A and B with different sizes of the unit mesh. With small mesh contents, they have 8- and 12-layer sequences along the z-axis, respectively, as shown in the table. With large mesh contents, they both have a 4-layer sequence along the x-direction with the stacking sequence ABAB.[6] For these structures, only the small meshes corresponding to the stacking along the z axis are shown in Figure 5.

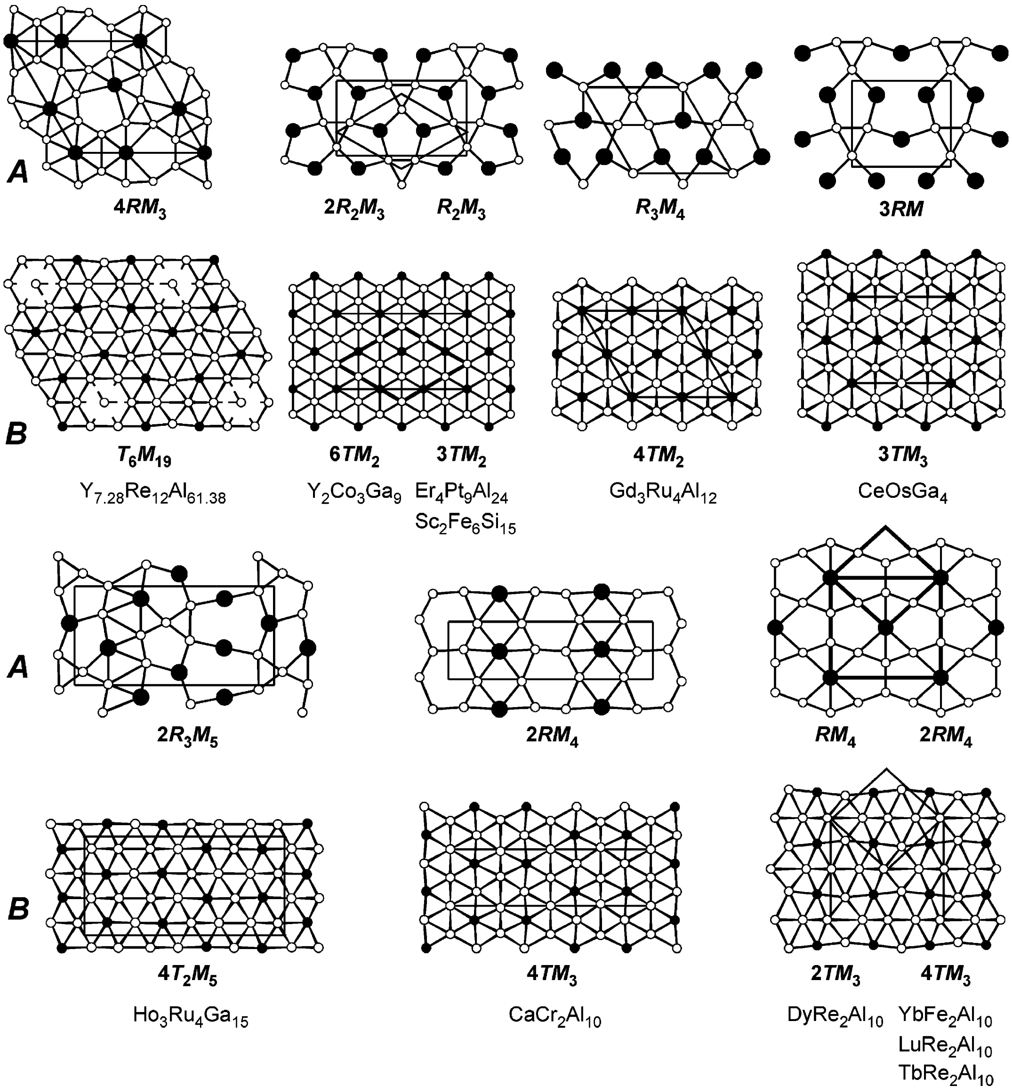

Figure 4. Atomic layers A and B of the $Y_{7.28}Re_{12}Al_{61.38}$ type structure as compared to the corresponding layers in various other structures of $R_xT_yM_z$ compounds with layered topology (R = Ca and rare earth elements, T = Cr and late transition metals, M = Si, Al, and Ga). In the upper left-hand corner, the layers of the $Y_{7.28}Re_{12}Al_{61.38}$ type structure are shown. One unit mesh of the A layers in this structure contains four formula units YAl_3 ($4RM_3$). The B layers of this structure have a unit mesh content of Re_6Al_{19} (T_6M_{19}). In this, like in most other structures of this structural family with layered topology, layers of types A and B alternate, resulting in the ideal formula $Y_8Re_{12}Al_{62}$ [(2 × $4YAl_3$) + (2 × Re_6Al_{19})]. The layers of the other structures are drawn analogously. Layers of type A are flat and loosely packed. Layers of type B consist of hexagonal close-packed atoms. They are slightly puckered. Further details may be gathered from Table 5.

hedrally close-packed structures of which the σ-phase, the β-W (W_3O_{1-x}, Cr_3Si, A15) type phases, and the Laves phases are probably the best known examples.[18−20] The metals with hexagonal or cubic close-packed structures are ductile. In contrast, the intermetallics with tetrahedrally close-packed structures are brittle and can easily be ground to powders. This is also the case for the intermetallics discussed here.

Table 5 lists all of the examples which we have recognized as belonging to this structural family. They are arranged in this table according to the content of the main group elements M (mostly aluminum or gallium, but also silicon, and furthermore, some of these structure types may have representatives with other M components, e.g., $Ca_3Rh_4In_{12}$ has $Gd_3Ru_4Al_{12}$ type structure[33]). This table also lists the space group, the cell content *Z*, the stacking sequence, and the references to the original structure determinations, as well as to the publications where the common building principle has been recognized. It can be seen that in most structures the layers of type A and the layers of type B alternate. Exceptions are the structure of $Er_4Pt_9Al_{24}$ with the stacking sequence ABBAB and the structure of $Sc_{1.2}Fe_4Si_{9.8}$ with the stacking sequence ABBABB. In all of these structures, the layers of type A are flat and relatively loosely packed. They contain all of the large electropositive atomic components R (mostly rare earth elements) and, in addition, a portion of the main group elements M. The layers of type B are always hexagonal close-packed, but slightly puckered. They contain all of the transition metal atoms T and the remaining portion of the main group elements. The structures of $Gd_3Ru_4Al_{12}$,[21] $Y_2Co_3Ga_9$,[22] and $CaCr_2Al_{10}$[26] have been known for some time, but their belonging to this family of layered structures has been recognized only recently.[6,23,27] Another recent addition to this family of structures with layered topology is the structure of $Y_2Pt_6Al_{15}$.[9] This structure is an ordered superstructure with a hexagonal subcell first determined for the silicide $Sc_{1.2}Fe_4Si_{9.8}$.[24] In Figure 4, the various layers of types A and B of this structural family are shown together with the formulas giving the contents of the unit meshes and the structure types.

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Supporting Information Available: Further crystallographic details and X-ray crystallographic files of $Y_{7.86}Os_{12}Al_{61.51}$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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