Cd_4 Tetrahedra and Condensed RE_6Rh Trigonal Prisms as Building Units in the Rare Earth-rich Compounds $RE_{15}Rh_5Cd_2$ (RE = La, Ce, Pr, Nd)

Frank Tappe, Ute Ch. Rodewald, Rolf-Dieter Hoffmann, and Rainer Pöttgen

Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstraße 30,
48149 Münster, Germany

Reprint requests to R. Pöttgen. E-mail: pottgen@uni-muenster.de

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The rare earth-rich compounds $RE_{15}Rh_5Cd_2$ (RE = La, Ce, Pr, Nd) were synthesized by induction melting of the elements in sealed tantalum tubes and characterized by X-ray powder diffraction. The structure of $La_{15}Rh_5Cd_2$ was refined from single-crystal diffractometer data: new type, $R3m$, a = 1016.4(2), c = 4418.7(9) pm, $wR2$ = 0.0417, 2258 F^2, 95 variables. Striking structural motifs in the $RE_{15}Rh_5Cd_2$ intermetallics are rhodium-centered trigonal prisms RE_6Rh which are condensed *via* common corners and edges to a complex three-dimensional network which leaves cavities for Cd_4 tetrahedra and RE_6 octahedra. The structural relationship with the recently discovered structure types Gd_4RhIn and $Pr_{23}Ir_7Mg_4$ is discussed.

Key words: Intermetallics, Metal-rich Compounds, Crystal Structure

Introduction

The rare earth-rich parts of the RE-T-Mg(Cd) (RE = rare earth element; T = transition metal) phase diagrams have intensively been studied in recent years. Two large series of compounds have been discovered, *i. e.* RE_4TMg(Cd) (T = Co, Ni, Ru, Rh, Pd, Ir, Pt) [1 – 9] with the cubic Gd_4RhIn [10] type structure and $RE_{23}T_7X_4$ (T = Ni, Ru, Rh, Pt; X = Mg, Cd) [4, 8, 11 – 16] with the hexagonal $Pr_{23}Ir_7Mg_4$ [4] or $Yb_{23}Cu_7Mg_4$ [17] type. Common structural motifs of the three structure types are three-dimensional networks of condensed RE_6T trigonal prisms and Mg_4, respectively Cd_4 tetrahedra. The latter are rare building groups in intermetallic compounds. The hydrogen uptake and the magnetic properties of selected compounds have been investigated. The 92 K antiferromagnet Gd_4NiMg absorbs up to 11 hydrogen atoms per formula unit [9]. The hydrogenation destroys the long-range magnetic ordering, and Gd_4NiMgH_{11} remains paramagnetic down to 1.8 K. Furthermore, the solid solution $Gd_4NiMg_{1-x}Al_x$ ($0 \leq x \leq 0.9$) shows a transition from antiferromagnetic ordering to cluster-glass behavior [18].

The RE_4TMg compounds show some flexibility in the electron count. Besides full substitution of the transition metal, also the rare earth element and the magnesium atoms can be substituted. Recent studies have shown the existence of significant solid solutions $RE_4NiMg_{1-x}Al_x$ ($0 < x < 0.9$) and $RE_{4-y}NiMg_{1+y}$ ($0 < y < 0.5$) with RE = Gd and Y [19].

Magnetic susceptibility measurements revealed quite high temperatures for magnetic ordering of the rare earth moments for RE_4CoCd and RE_4RhCd (RE = Tb, Dy, Ho), with the maximum value of 54 K for Tb_4CoCd [20]. In contrast, the more complex $RE_{23}T_7Mg_4$ and $RE_{23}T_7Cd_4$ compounds show much lower ordering temperatures [11, 12, 14 – 16], if at all.

Further phase analytical studies in the RE-T-Mg systems led to the lanthanum-rich compound $La_{43}Ni_{17}Mg_5$ [21] with completely different structural features. $La_{43}Ni_{17}Mg_5$ contains anti-Mackay polyicosahedral cluster units. Along with La_4NiMg (66.6 at.-% La : 16.6 at.-% Ni : 16.6 at.-% Mg) and $La_{23}Ni_7Mg_4$ (67.6 : 20.6 : 11.8), $La_{43}Ni_{17}Mg_5$ (66.2 : 26.2 : 7.7) is the third metal-rich compound in the La-Ni-Mg system, with all three having an almost equal lanthanum content. Our parallel work in the cadmium-based systems now led to a new series of compounds with composition $RE_{15}Rh_5Cd_2$ (RE = La, Ce, Pr, Nd; 68.2 : 22.7 : 9.1), which are structurally closely related to the Gd_4RhIn and $Pr_{23}Ir_7Mg_4$ types. The preparation and structure determination of these intermetallics are reported herein.

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Table 1. Lattice parameters (Guinier powder data) of the ternary cadmium compounds $RE_{15}Rh_5Cd_2$.

Compound	*a* (pm)	*c* (pm)	*V* (nm^3)
$La_{15}Rh_5Cd_2$	1016.4(2)	4418.7(9)	3.9533
$Ce_{15}Rh_5Cd_2$	1003.2(4)	4348.5(14)	3.7901
$Pr_{15}Rh_5Cd_2$	996.7(3)	4331.8(11)	3.7267
$Nd_{15}Rh_5Cd_2$	990.8(2)	4299.0(11)	3.6549

Table 2. Crystal data and structure refinement for $La_{15}Rh_5Cd_2$ (space group $R3m$, $Z = 6$).

Empirical formula	$La_{15}Rh_5Cd_2$
Unit cell dimensions	Table 1
Molar mass, g mol^{-1}	2823.00
Calculated density, g cm^{-3}	7.12
Crystal size, μm^3	$10 \times 20 \times 60$
Transm. ratio (max / min)	0.743 / 0.493
Absorption coeff., mm^{-1}	28.3
Detector distance, mm	80
Exposure time, min	8
ω range; increment, deg.	0 – 180, 0.8
Integr. param. A, B, EMS	13.0; 3.0; 0.012
$F(000)$, e	7056
θ range, deg.	2 – 27
Range in *hkl*	± 12, ± 12, ± 56
Total no. reflections	10091
Independent reflections / R_{int}	2258 / 0.0638
Reflections with $I \geq 2\sigma(I)$ / R_σ	1406 / 0.1225
Data / parameters	2258 / 95
Goodness-of-fit on F^2	0.559
$R1$ / $wR2$ for $I \geq 2\sigma(I)$	0.0275 / 0.0383
$R1$ / $wR2$ for all data	0.0523 / 0.0417
Flack parameter	$-0.01(5)$
Extinction coefficient	0.0000095(11)
Largest diff. peak / hole, e Å^{-3}	6.08 / -1.85

Experimental Section

Synthesis

Starting materials for the synthesis of the $RE_{15}Rh_5Cd_2$ samples were ingots of the rare earth metals (Johnson Matthey or smart elements), rhodium powder (Degussa-Hüls) and a cadmium rod (Johnson-Matthey), all with stated purities better than 99.9 %. Pieces of the rare earth ingots were first arc-melted [22] to small buttons under an argon atmosphere. The argon was purified before with molecular sieves, silica gel, and titanium sponge (900 K). Next the rare earth buttons, the rhodium powder and pieces of the cadmium rod (a 15 : 5.2 : 1.8 atomic ratio was chosen to suppress formation of the $RE_{23}Rh_7Cd_4$ phases) were sealed in tantalum tubes under an argon pressure of *ca.* 800 mbar. The ampoules were placed in a water-cooled sample chamber of a high-frequency furnace (Hüttinger Elektronik, Freiburg, type TIG 1.5/300) under flowing argon [23], first heated to about 1473 K and kept at that temperature for 5 min. The temperature was then lowered within 1 min to 923 K, and the tubes were annealed for another 3 h. Finally the tubes were quenched to r. t. The temperature was controlled through a Sensor Therm Methis MS09 pyrometer with an accuracy of ±30 K. All samples could easily be separated from the ampoules by mechanical fragmentation. No reaction with the container material was observed. The polycrystalline samples deteriorate slowly in air.

For crystal growth of $La_{15}Rh_5Cd_2$ and other $RE_{15}Rh_5Cd_2$ samples the reactions were carried out in a muffle furnace instead, with the sealed tantalum tubes enclosed in evacuated quartz tubes for oxidation protection. The samples were heated to 1473 K within 4 h and kept at this temperature for another 4 h. Thereafter the tubes were slowly cooled down to 673 K within 8 d. After another 8 d of annealing at this temperature the furnace was switched off and cooled to r. t. by radiative heat loss. The resulting small single crystals exhibit metallic lustre, while the ground powder is dark grey.

EDX data

Semiquantitative energy-dispersive analyses of X-rays (EDX) of the crystals investigated on the diffractometer and of the bulk samples were carried out by use of a Zeiss EVO® MA10 scanning electron microscope in variable pressure mode with the rare earth trifluorides, CeO_2, rhodium and cadmium as standards. The bulk samples were embedded in a methylmetacrylate matrix, and the surface was polished with diamond and silica paste. The surface remained unetched for the EDX measurements. The experimentally observed compositions were close to the ideal one. No impurity elements heavier than sodium (detection limit of the instrument) have been found.

X-Ray diffraction

The $RE_{15}Rh_5Cd_2$ samples were characterized by Guinier patterns (image plate detector, Fuji-film BAS-1800 readout system) with Cu$K_{\alpha 1}$ radiation and α-quartz (a = 491.30 and c = 540.46 pm) as the internal standard. The hexagonal lattice parameters (Table 1) were refined by a least-squares routine. Correct indexing was ensured through intensity calculations [24].

Small single crystals of $La_{15}Rh_5Cd_2$ and other $RE_{15}Rh_5Cd_2$ samples were isolated from the crushed samples prepared in the muffle furnace. They were glued to quartz fibers and investigated on a Buerger precession camera (white Mo radiation, Fuji-film imaging plate) in order to check the quality for intensity data collection. The data sets were collected at r. t. by use of an IPDS II diffractometer (graphite-monochromatized MoK_α radiation; oscillation mode). Numerical absorption corrections were applied to the data sets. Details on the crystallographic data are given in Table 2.

Structure refinement

The diffractometer data sets showed hexagonal lattices, and only the systematic extinction for an *R* centering, lead-

Table 3. Atomic coordinates and isotropic displacement parameters (pm^2) for $La_{15}Rh_5Cd_2$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	W. position	*x*	*y*	*z*	U_{eq}
La1	9*b*	0.12616(11)	−*x*	0.19347(3)	118(4)
La2	9*b*	0.13223(10)	−*x*	0.04187(3)	109(4)
La3	9*b*	0.20536(10)	−*x*	0.11775(3)	109(3)
La4	9*b*	0.20935(11)	−*x*	0.26750(4)	150(4)
La5	9*b*	0.45880(10)	−*x*	0.33878(3)	124(4)
La6	9*b*	0.54020(10)	−*x*	0.07612(3)	106(4)
La7	9*b*	0.54158(10)	−*x*	0.21773(3)	104(3)
La8	9*b*	0.79248(10)	−*x*	0.29049(3)	112(4)
La9	9*b*	0.79346(11)	−*x*	0.14649(4)	114(4)
La10	3*a*	0	0	0.11208(6)	91(6)
La11	3*a*	0	0	0.26607(6)	106(6)
La12	3*a*	0	0	0.52232(6)	104(6)
Rh1	9*b*	0.47832(13)	−*x*	0.15352(5)	140(5)
Rh2	9*b*	0.52017(14)	−*x*	0.41180(5)	133(5)
Rh3	9*b*	0.85711(13)	−*x*	0.23132(5)	156(5)
Rh4	3*a*	0	0	0.99994(8)	120(8)
Cd1	9*b*	0.43848(12)	−*x*	0.00113(5)	116(4)
Cd2	3*a*	0	0	0.39207(8)	113(7)

ing to space groups $R\bar{3}m$, $R3m$, $R\bar{3}$, $R32$, and $R3$, of which the non-centrosymmetric group $R3m$ was found to be correct during structure refinement. The $La_{15}Rh_5Cd_2$ data set was calculated first. The starting atomic parameters were deduced by Direct Methods with SHELXS-97 [25], and the structure was refined using SHELXL-97 [26] (full-matrix least-squares on F^2) with anisotropic atomic displacement parameters for all sites. The occupancy parameters were refined in separate series of least-squares cycles in order to check for deviations from the ideal composition. No significant deviations were observed, and in the final cycles the ideal values were assumed again. The refined positional parameters and interatomic distances are listed in Tables 3 and 4.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-422833.

Table 4. Interatomic distances (pm) of $La_{15}Rh_5Cd_2$ calculated with the powder lattice parameters. Standard deviations are all equal or smaller than 0.3 pm.

La1: 2	Rh3	291.0	La4: 1	Cd1	348.2	La8: 1	Rh3	285.2	Rh1: 2	La3	288.8
1	La4	358.4	1	La1	358.4	1	Rh4	291.2	2	La9	294.5
1	La3	362.5	2	Rh3	363.3	2	Cd1	371.3	1	La12	299.5
1	La12	365.3	1	La11	368.6	1	La2	374.5	1	La7	304.8
2	Rh1	369.1	2	La4	378.1	2	La4	380.8	1	La6	358.9
2	La9	379.3	2	La8	380.8	1	La11	380.9	2	La1	369.1
2	La7	381.1	2	La5	384.0	2	La8	383.6	Rh2: 2	La6	290.9
2	La1	384.7	2	La7	387.8	2	La5	384.0	2	La2	294.6
1	La11	390.2	1	La12	409.9	2	La7	390.1	1	La10	297.6
1	La10	422.7	La5: 1	Rh2	340.3	La9: 2	Rh1	294.5	1	La9	318.6
La2: 2	Rh2	294.7	2	Cd1	349.0	1	Rh2	318.6	1	La5	340.3
1	Rh4	297.5	2	La2	358.9	2	La1	379.3	2	La3	366.2
2	Cd1	355.6	1	Rh4	366.8	2	La6	382.6	Rh3: 1	La8	285.2
2	La5	358.9	2	La5	382.6	2	La3	384.2	2	La1	291.1
1	La3	359.2	2	La6	383.0	2	La7	385.0	1	La11	294.7
1	Cd2	361.8	2	La4	384.0	2	La9	386.6	2	La7	301.1
1	La8	374.5	2	La8	384.0	1	Rh3	391.2	2	La4	363.3
1	La10	387.9	La6: 2	Rh2	290.9	1	La10	394.1	1	La9	391.2
2	La6	389.8	1	Rh1	358.9	La10: 3	Rh2	297.6	Rh4: 3	La8	291.2
2	La2	403.2	2	La3	367.7	3	La3	362.4	3	La2	297.5
La3: 2	Rh1	288.8	1	Cd2	372.2	3	La2	387.9	3	La5	366.8
1	Cd2	344.6	1	Cd1	376.7	3	La9	394.1	Cd1: 1	Cd2	314.7
1	La2	359.2	2	La9	382.6	3	La1	422.7	2	Cd1	320.6
1	La10	362.4	2	La5	383.0	La11: 3	Rh3	294.7	1	La4	348.2
1	La1	362.5	2	La6	385.6	3	Cd1	354.4	2	La5	349.0
2	Rh2	366.2	2	La2	389.8	3	La4	368.6	1	La11	354.4
2	La6	367.7	La7: 2	Rh3	301.1	3	La8	380.9	2	La2	355.6
2	La9	384.2	1	Rh1	304.8	3	La1	390.2	2	La8	371.3
1	La12	387.1	2	La1	381.1	La12: 3	Rh1	299.5	1	La6	376.7
2	La3	390.2	2	La7	381.4	3	La1	365.3	Cd2: 3	Cd1	314.7
			2	La9	385.0	3	La3	387.1	3	La3	344.6
			2	La4	387.8	3	La7	388.0	3	La2	361.8
			1	La12	388.0	3	La4	409.9	3	La6	372.2
			2	La8	390.1						

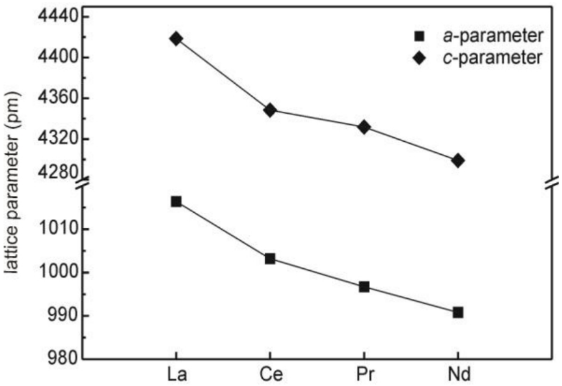


Fig. 1. Course of the lattice parameters in the series of $RE_{15}Rh_5Cd_2$ compounds.

Structure refinements were carried out also for the other three compounds. All crystals of the $RE_{15}Rh_5Cd_2$ compounds were more or less intergrown, and for the cerium, praseodymium, and neodymium compounds also small additional domains of different compounds were detected on the image plate diffractometer. The integrated data sets clearly confirmed the structural model obtained for the lanthanum compound, however, the crystal quality did not allow for further details. The refinements resulted in too high residuals and also unreasonable residual peaks in the final difference Fourier maps.

Discussion

The rare earth-rich intermetallic compounds $RE_{15}Rh_5Cd_2$ (RE = La, Ce, Pr, Nd) crystallize with a new structure type. The cell parameters decrease from the lanthanum to the neodymium compound as expected from the lanthanoid contraction. The cerium compound smoothly fits in the Iandelli plot (Fig. 1), indicating stable trivalent cerium in $Ce_{15}Rh_5Cd_2$. In the following discussion we concentrate on the $La_{15}Rh_5Cd_2$ structure which was refined on the basis of single crystal data.

A view of the $La_{15}Rh_5Cd_2$ structure approximately along the [110] direction is presented in Fig. 2. The four crystallographically independent rhodium atoms all have trigonal prismatic lanthanum coordination at La–Rh distances ranging from 285 to 319 pm, close to the sum of the covalent radii [27] of 294 pm. The short La–Rh distances are indicative of strong La–Rh bonding, similar to the La–Co and La–Ru bonding in the trigonal prisms of the closely related compounds La_4CoMg [1] and La_4RuMg [3].

The La_6Rh trigonal prisms are condensed *via* common corners and egdes forming a complex three-dimensional network which leaves large cavities. The latter are filled with La_6 octahedra (medium-grey shading in Fig. 2) formed by the La4 atoms (the lanthanum atoms which have no close contacts to rhodium) and Cd_4 tetrahedra (light-grey shading). These tetrahedra are all oriented in one direction, leading to the non-centrosymmetric space group. The Cd_4 tetrahedra are formed by the crystallographically independent Cd1 (9*b*) and Cd2 (3*a*) atoms. They are slightly compressed with Cd–Cd distances of 315 and 321 pm, in good agreement with the Cd–Cd distances in *hcp* cadmium (6×298 and 6×329 pm) [28].

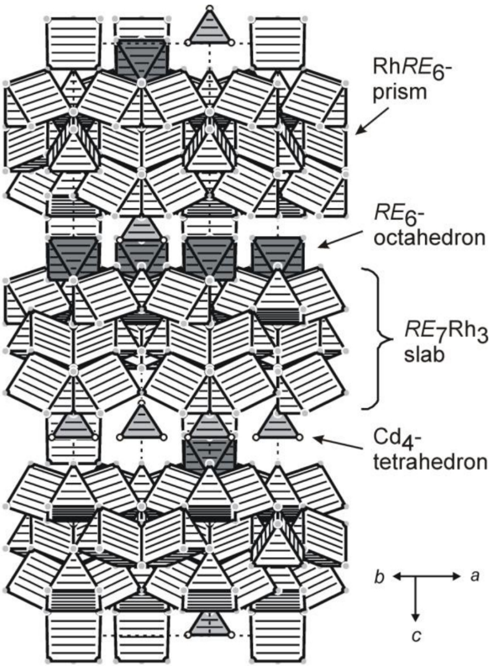
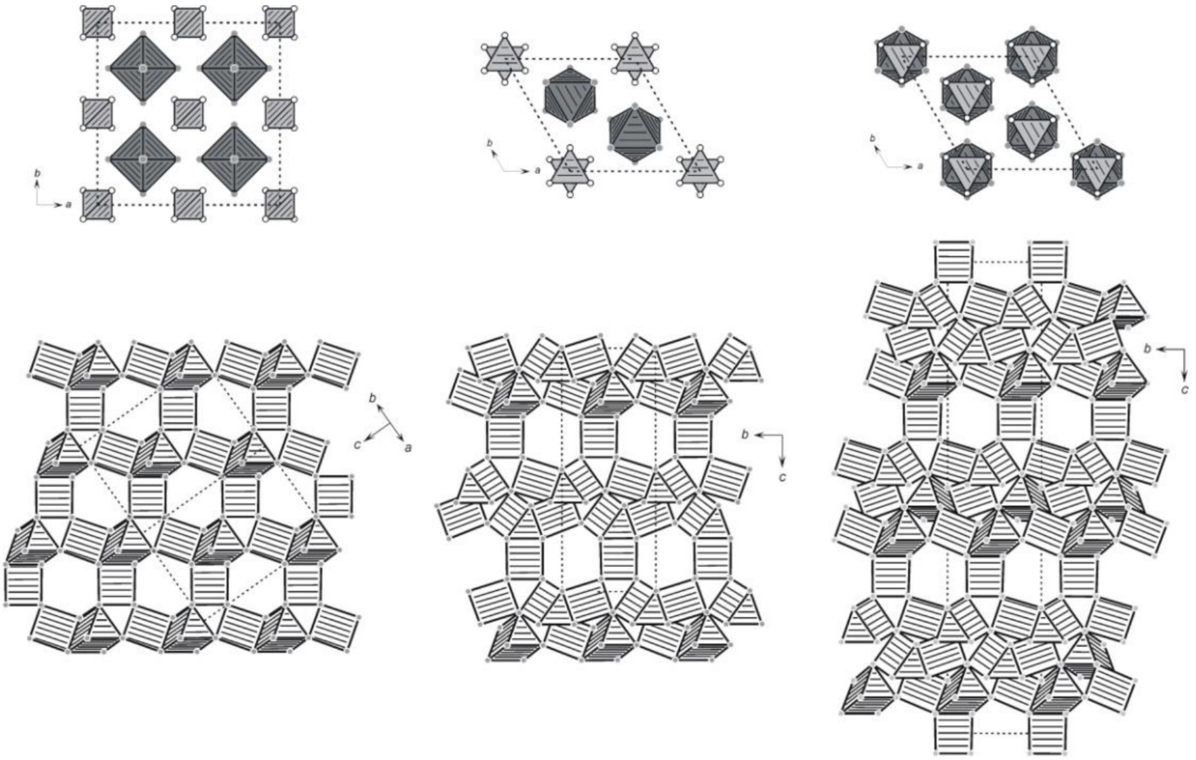


Fig. 2. View of the $RE_{15}Rh_5Cd_2$ structure approximately along the [110] direction. The network of condensed trigonal RE_6Rh prisms, the Cd_4 tetrahedra and the empty RE_6 octahedra (medium grey shading) are emphasized. For clarity, not all Cd_4 tetrahedra and RE_6 octahedra are drawn in all layers. For details see text.

The crystal chemical features described above are reminiscent of the recently discovered metal-rich structure types Gd_4RhIn [10] and $Pr_{23}Ir_7Mg_4$ [4] which both have several cadmium-containing representatives RE_4TCd [6, 7] and $RE_{23}T_7Cd_4$ [13, 14]. The three structure types are compared in Fig. 3. In the upper drawings we present the arrangement of the RE_6 octahedra and the In_4, respectively Mg_4 and Cd_4 tetrahedra in the unit cells, while the networks of condensed transition metal centered trigonal



Gd_4RhIn, $F\bar{4}3m$ $Pr_{23}Ir_7Mg_4$, $P6_3mc$ $La_{15}Rh_5Cd_2$, $R3m$

Fig. 3. Comparison of the structure types Gd_4RhIn, $Pr_{23}Ir_7Mg_4$, and $La_{15}Rh_5Cd_2$. The top drawing shows the arrangement of the In_4 (Mg_4, Cd_4) tetrahedra and empty RE_6 octahedra while the networks of condensed trigonal RE_6T prisms are compared in the bottom drawing.

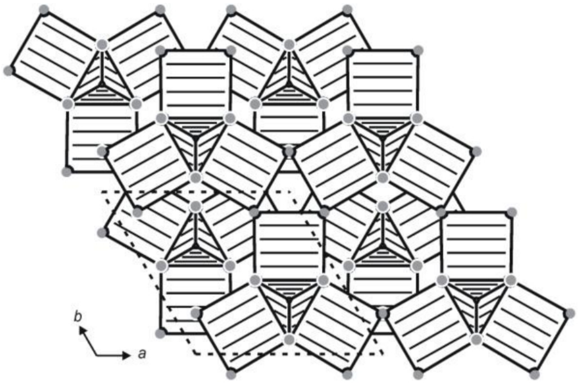


Fig. 4. A double layer of condensed trigonal La_6Rh prisms in the structure of La_7Rh_3 (Th_7Fe_3 type).

prisms are shown at the bottom. In the series of compositions 16-4-4 (*i. e.* 4-1-1), 23-7-4, and 30-10-4 (*i. e.* 15-5-2), one formally adds a formula unit RE_7T_3 in each step. This is easily visible in Fig. 3. In the sequence $Gd_4RhIn \rightarrow Pr_{23}Ir_7Mg_4 \rightarrow La_{15}Rh_5Cd_2$ one adds a further layer of condensed RE_6T prisms. It is interesting to note that many binary Th_7Fe_3 type intermetallics RE_7T_3 [29–32] with an almost equal condensation pattern are known. As an example we present a cutout of the La_7Rh_3 structure [32] in Fig. 4.

Although $Yb_{23}Cu_7Mg_4$ [17] has the same composition as $Pr_{23}Ir_7Mg_4$ [4], it adopts its own structure type, for which so far no other representatives have been reported. $Yb_{23}Cu_7Mg_4$ has a different stacking pattern for the sub-layers of condensed prisms [8].

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