

Electron-poor polar intermetallics: A case study within the system Rb-Hg-In

Marco Wendorff, Caroline Röhr

Institut für Anorganische und Analytische Chemie, Albert-Ludwigs-Universität Freiburg, Freiburg, Germany



Polar intermetallics A_xM_y of the alkali elements Na to Cs (A) with $v.e./M < 3$ are indeed rare, but highly interesting, as their predominantly complex singular structures no longer follow simple electron counting rules (WADE/ZINTL/*mno*). The ternary system Rb–Hg–In is one of the few systems offering ideal conditions for investigating crystal chemistry and bonding of polyanion networks with $v.e./M = 2 - 3$:

- binary mercurides known [1-3].
- ideal radius ratio $r_{Rb^+} : r_M$ for space tiling of $[Rb@M_n]$ [$n=12-18$] ccp's (yellow), empty icosahedra (clusters) (bluish, high $v.e./M$) and local M prisms/t.p. (green/red, lower $v.e./M$).
- χ and $\Delta\chi$ of Rb/Hg/In ideal to gain not only $A-M$ but – due to polyanion 'coloring' – also $M-M$ COULOMB interactions.

Boron-related cluster compounds (v.e./M ~ 3)

Close to the 'boron-border' of $v.e./M=3$, complex condensed cluster structures are formed, in the title system Rb–Hg–In the hexagonal $Na_8K_{23}Cd_{12}In_{48}$ [4] (also called $Ca_6Cu_6Al_6$ -type and the large new orthorhombic structure of $Rb_{42}Hg_{26}In_{105}$ (crystal data cf. Table 1). In both phases, the M polyanions consist of empty (!) icosahedra (Fig. 2/3: dark blue), which are connected via exo-bond to form KAGOME-nets. These nets are AA stacked, which

allows to topologically connect both structures with the $CaCu_5$ -type:

In the hexagonal phase, the second Cu position of this structure is occupied by In_3 -triangles consisting of four-bonded In atoms. The Ca position (0,0,0) is occu-

pied by a Rb/Hg centered dimer of hexagonal antiprisms, which are capped by disordered Hg_3 triangles. This always heavily disordered structure region is similarly found in all isotopic ternary alkali/alkaline-earth Li/Mg/Cu/Ag/Au/Cd/Hg trielides.

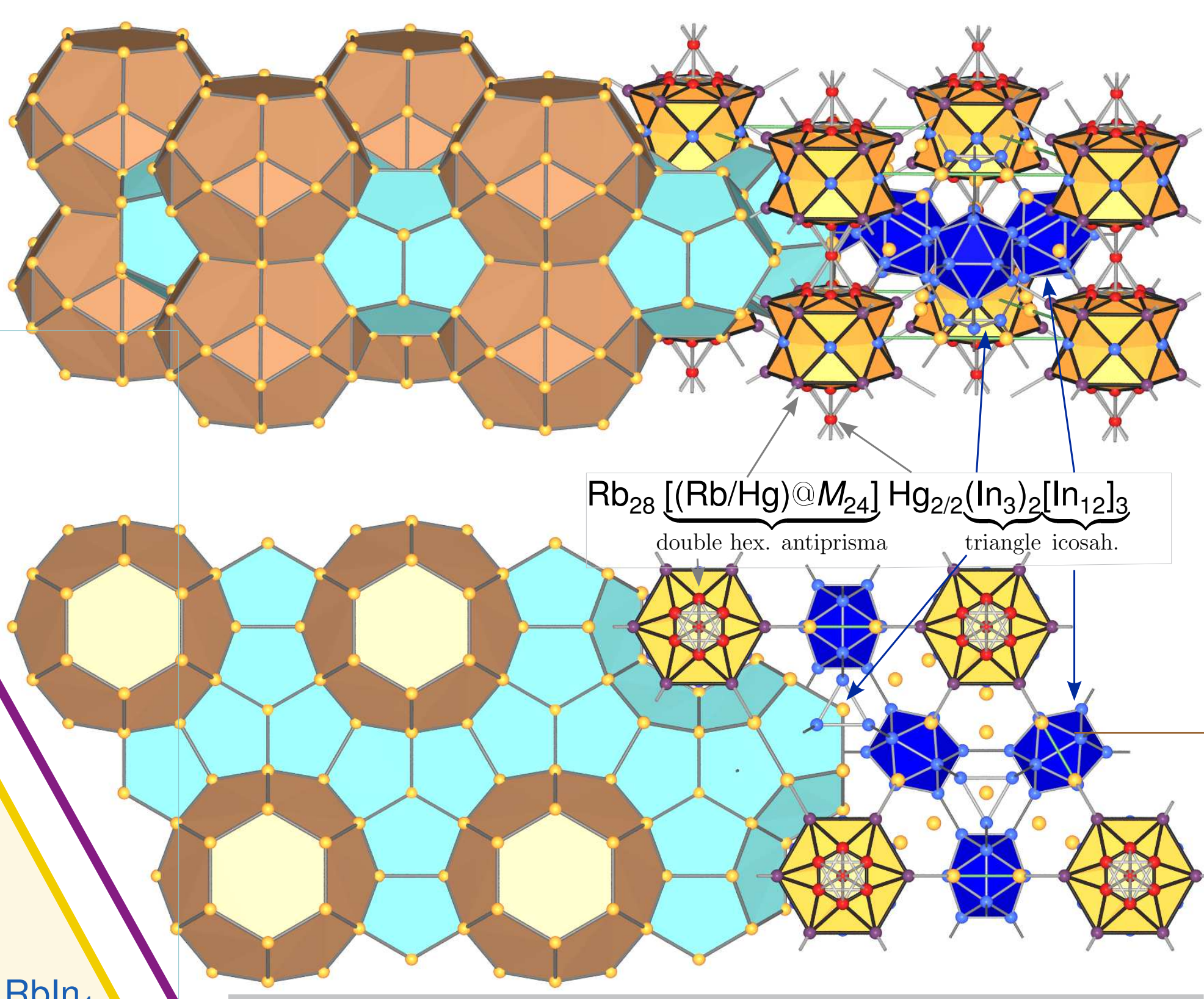


Fig. 2: Projection (bottom) and perspective view (top) of unit cell of $Rb_{28}Hg_{20}In_{47.1}$.

In the orthorhombic structure, the Cu(2) site is occupied by face-sharing icosahedra (double icosahedra M_{21} , Fig. 3, cyan). The Ca position is taken by a pair of such M_{21} double-icosahedra (magenta). All (double)icosahedra are connected via exo-bonds. A small number of additional 5-6 bonded Hg/In atoms are connecting the Hg/In icosahedral clusters in addition.

Compound	$Rb_{28.6}Hg_{20.3}In_{47.1}$	$Rb_{42}Hg_{26.2}In_{104.8}$
Crystal system	hexagonal	orthorhombic
Space group	$P6/mmm$, no. 193	$Pbam$, no. 55
PEARSON symbol	$hP96$	$oP346$
Structure type	$Na_8K_{23}Cd_{12}In_{48}$	new
Lattice parameters [pm]	a b c	1795.0(2) 1764.8(2) 3176.7(5)
$V_{u.c.}$ [10^6 pm ³]	2986.8(7)	10467(2)
R Value	0.0653	0.0363

Table 1: Crystal data of $Rb_{28.6}Hg_{20.3}In_{47.1}$ and $Rb_{42}Hg_{26.2}In_{104.8}$.

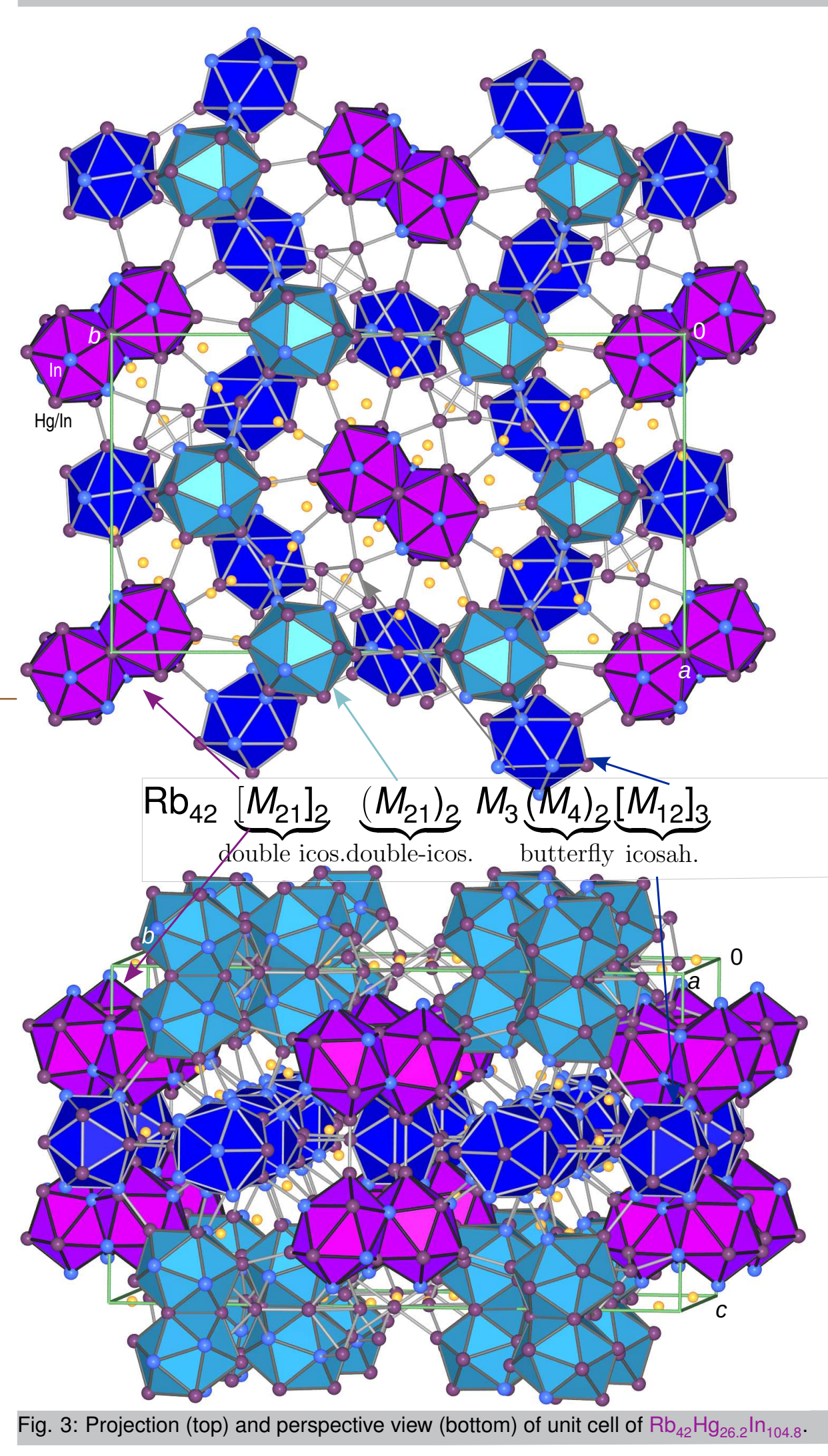


Fig. 3: Projection (top) and perspective view (bottom) of unit cell of $Rb_{42}Hg_{26.2}In_{104.8}$.

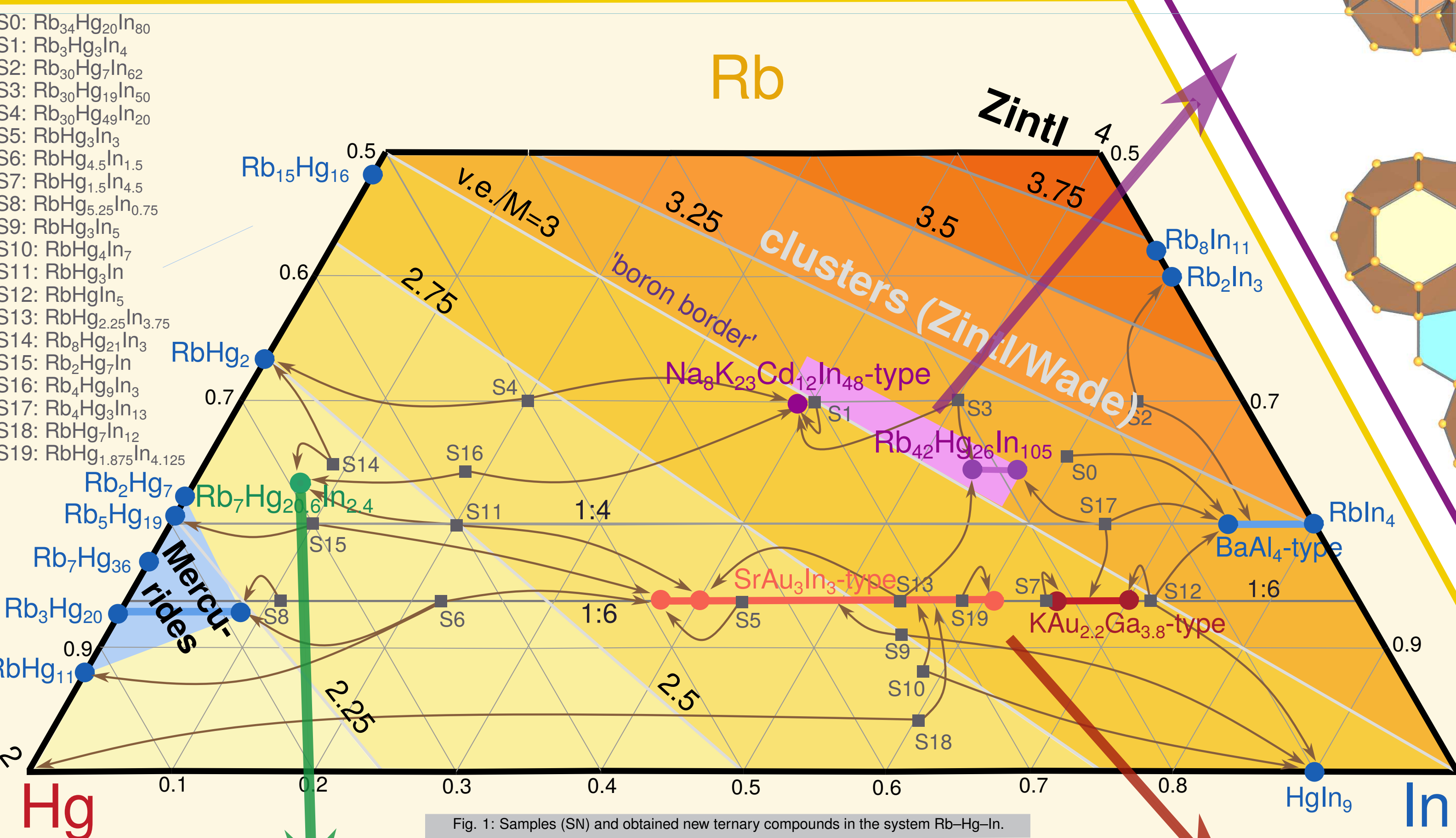


Fig. 1: Samples (SN) and obtained new ternary compounds in the system Rb–Hg–In.

$Rb_7Hg_{20.6}In_{2.4}$ (v.e./M=2.41)

Compound	$Rb_7Hg_{20.6}In_{2.4}$
Crystal system	monoclinic
Space group	$P2_1/c$, no. 14
PEARSON symbol	$sP120$
Structure type	new
Lattice parameters [pm, °]	a 1244.0(2) b 2319.6(3) c 1239.1(2) β 105.465(2)
$V_{u.c.}$ [10^6 pm ³]	3446.0(8)
R Value	0.0404

The new complex Hg-rich compound $Rb_7Hg_{20.6}In_{2.4}$ (crystal data cf. Table 4) contains 7 different Rb sites, 19 pure Hg positions and 4 Hg/In mixed sites with an approximately 1:1 ratio of Hg and In. The Hg/In polyanion exhibits similar trigonal prisms as observed in the 1:6 phases (green polyhedra) arranged around empty Hg/In cubes (Fig. 8 c). In addition sections of tetrahedra packings (t.p., red, Fig. 8 d) are present. Full space tiling is finally achieved together with the Rb ccp's [Rb-CN: 15+3 ($3\times$, cf. Fig. 8 e for Rb(2)), 15+2 ($3\times$) and 12+4 ($1\times$, FK-16 polyhedra)].

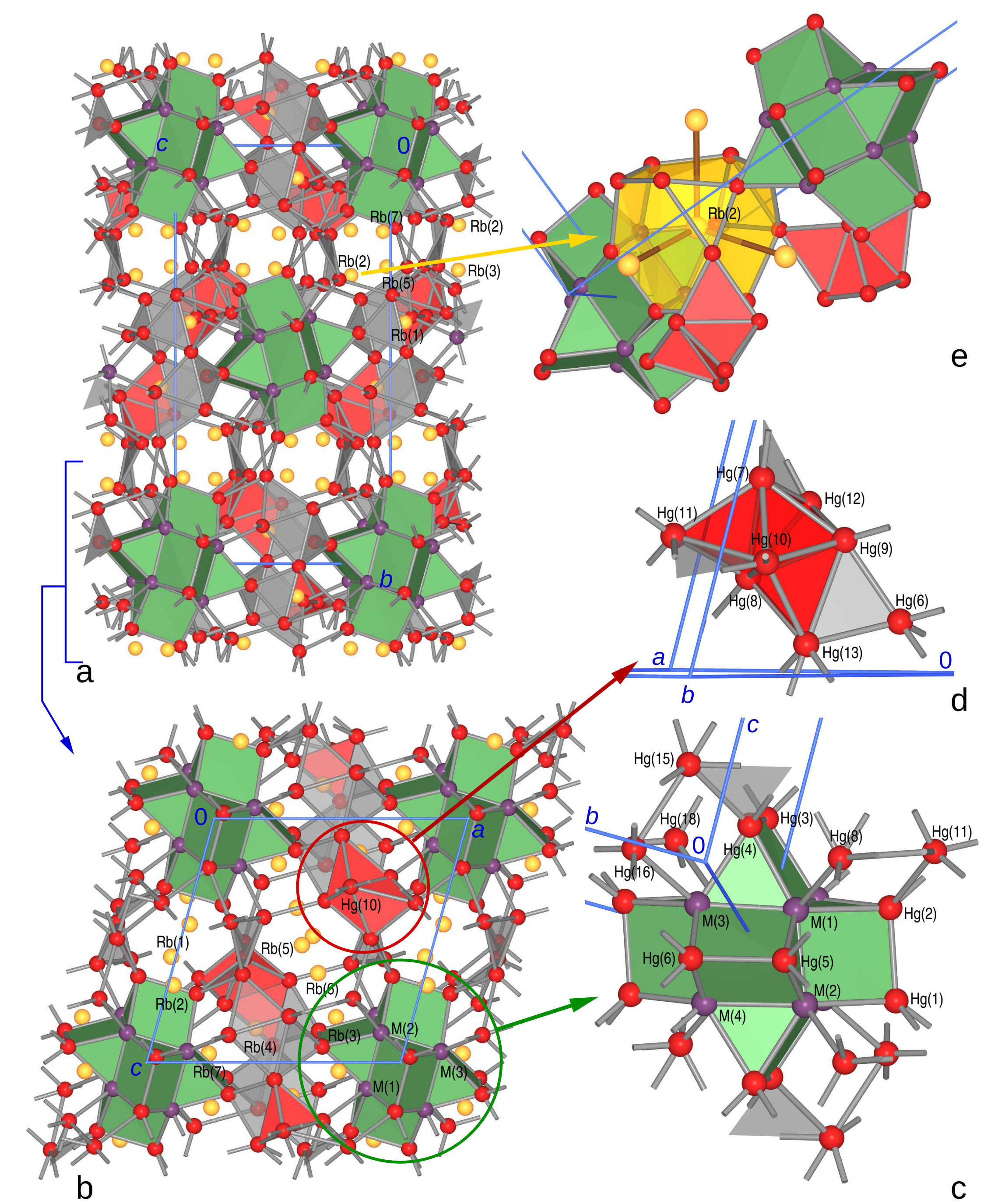


Fig. 8: Crystal structure of $Rb_7Hg_{20.6}In_{2.4}$: a: unit cell; b: $y=0.22$, $z=0.22$ cutout; c: empty Hg/In cube fused with 8 trigonal prisms; d: Hg₂-tetrahedra star as a section of the t.p.; e: Rb(2) ccp illustrating the characteristic Rb coordination.

$RbHg_{6-x}In_x$ (SrAu₄In₂- and KAu_{2.2}Ga_{3.8}-type; v.e./M=2.6 ... 2.98)

For the 1:6-phases $RbHg_{6-x}In_x$, the singular orthorhombic $SrAu_3In_3$ -type (light red [5,8], SG $Pmmn$) exhibits a broad phase width reaching from $x = 2.60$ ($v.e./M=2.60$) to $x = 4.29$. An increased In proportion leads to the formation of the $KAu_{2.2}Ga_{3.8}$ -type structure (SG $Immm$, dark red [6]), which shows a small phase width from $x = 4.46$ to $x = 4.87$ ($v.e./M=2.98$).

In both orthorhombic structures, which are connected by a k2 group-subgroup relation (cf. Fig. 4), mercury (partially) takes the gold positions of the basic structures.

Thus, the coloring in the polyanion is determined by an optimization of COULOMB contributions between the negatively charged Hg and the positively charge In atoms (BADER charges and volumes cf. Table 3). In the two structures, $[RbM_{20}]$ (6:8:6) ccp's (yellow polyhedra in Fig. 5 and 6) and face/edge-fused trigonal prisms $[M_6]$ (green) tile the space. Therewith, the two structures are closely related to those of binary and ternary $A^{III}M_{6/7/8}$ mercurides (like e.g. KHg_6 and $BaHg_6$ [7]) and can alternatively be described by an $|AB|$ stacking of $6.8^2+4.6.8$. (1:2) Hg/In nets (Fig. 6).

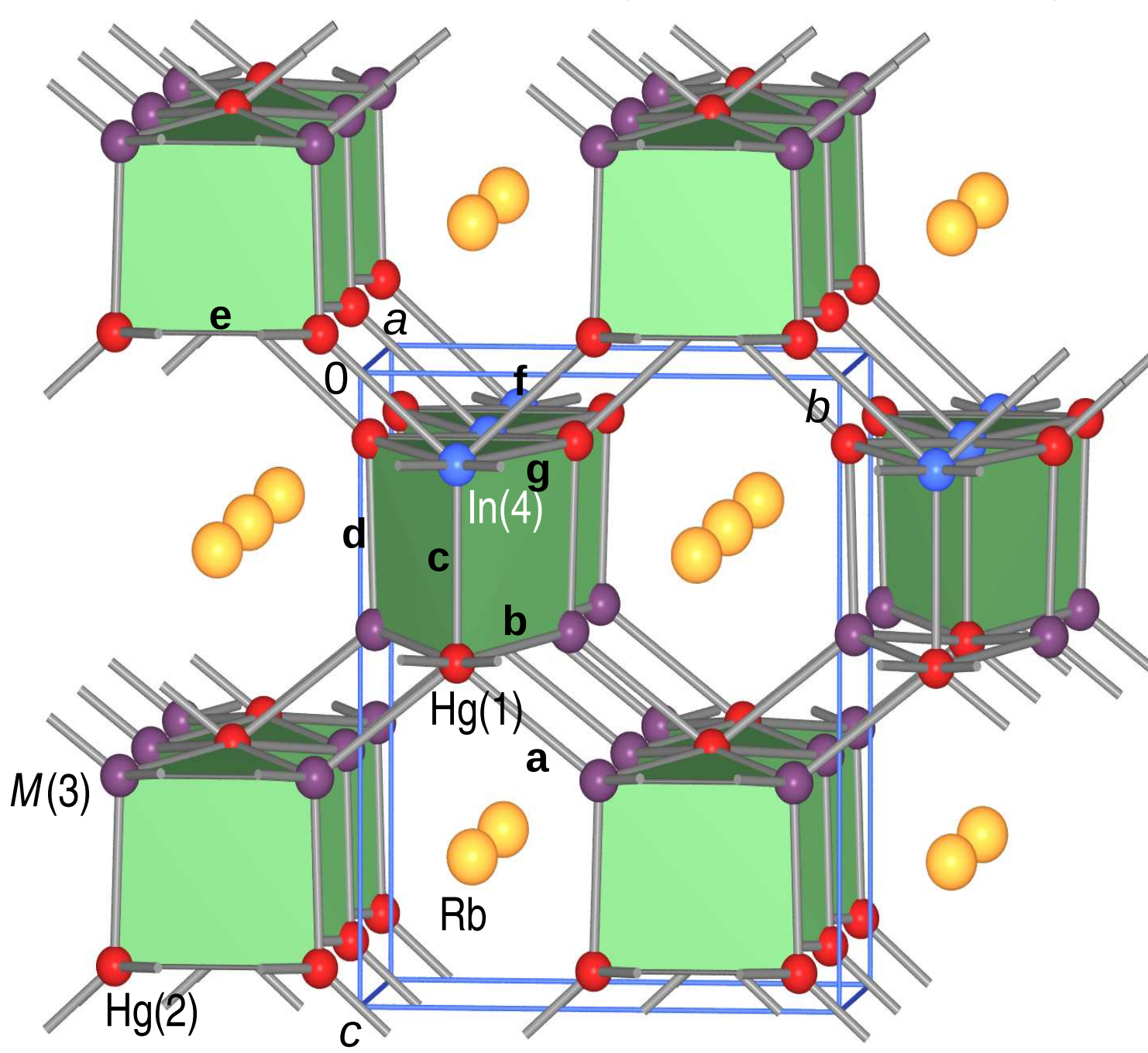


Fig. 5: Crystal structure of $RbHg_{3.4}In_{2.6}$ ($SrAu_3In_3$ -type).

Atom	Wyckoff position	atomic parameters			CN	V_{BB}	q
		x	y	z		[10^{-3} pm ³]	
Rb	2b	1/4	1/4	0.2458(2)	20 + 2 Rb	26.0	+0.709
Hg(1)	2a	1/4	3/4	0.4409(1)	7 + 4 Rb	29.1	-0.731
Hg(2)	4e	1/4	0.0268(9)	0.90956(8)	6 (+1) + 3 Rb	29.3	-0.430
Hg/In(3)	4e	1/4	0.4462(2)	0.6129(1)	5 (+4) + 3 Rb	25.3	+0.246
In(4)	2a	1/4	3/4	0.1273(2)	7 (+4) + 4 Rb	24.1	+0.413

Table 3: Atomic coordinates, CN and calculated BADER volumes/charges for $RbHg_{6-x}In_x$.

The calculated DOS of the model compound $RbHg_3In_3$ (Fig. 7), exhibits a broad minimum in the total DOS at E_F , which fits the observed v.e. numbers along the phase width x (magenta bar).

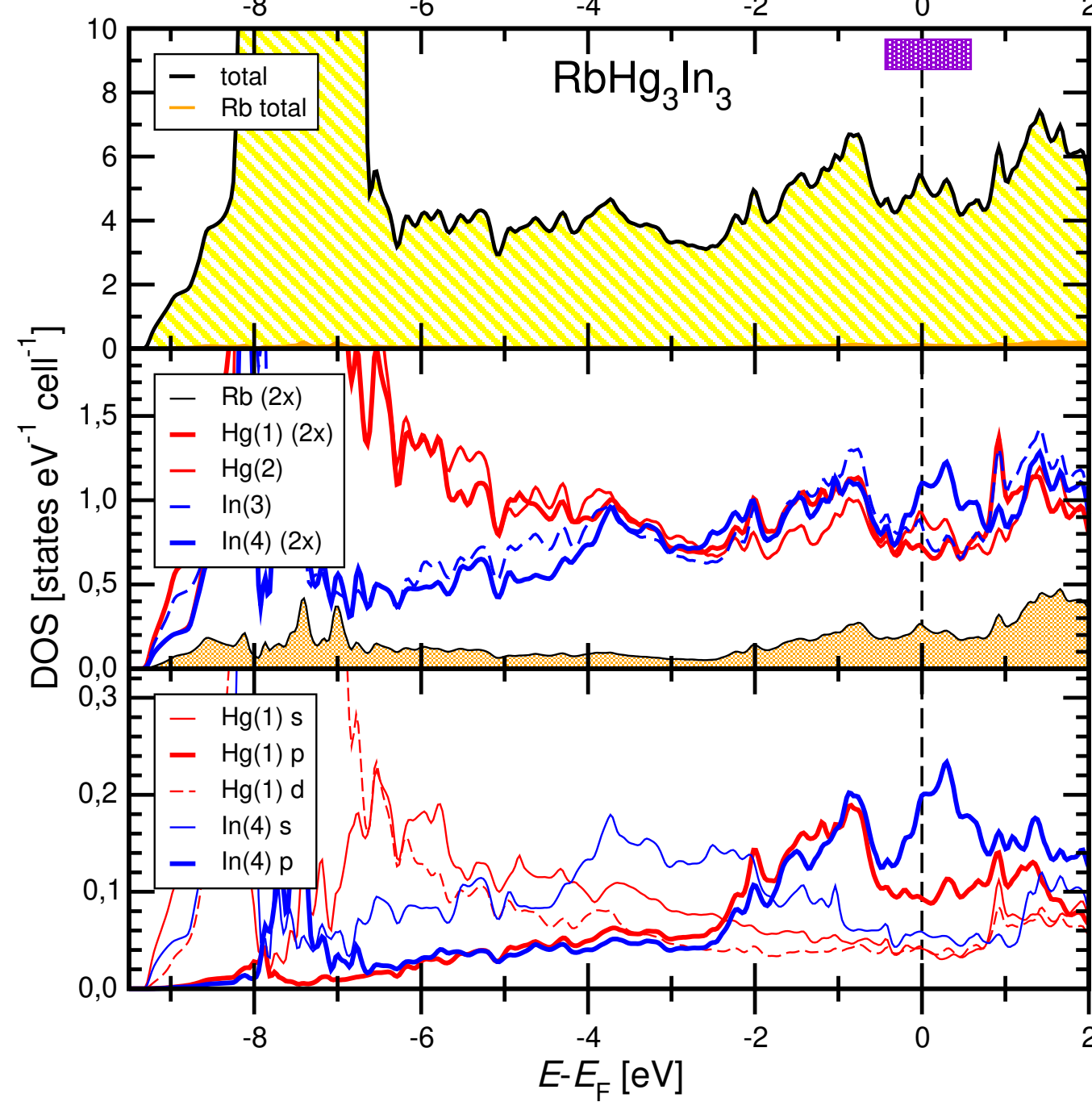


Fig. 7: Calculated total and partial DOS of $RbHg_3In_3$.

Compound	$RbHg_{3.4}In_{2.6}$	$RbHg_{1.7}In_{4.3}$	$RbHg_{1.54}In_{4.46}$	$RbHg_{1.13}In_{4.87}$
Crystal system		orthorhombic		
Space group	$Pmmn$, no. 59	$Immm$, no. 71		
PEARSON symbol	$oP14$	$oI14$		
Structure type	$SrAu_3In_3$ [5]	$KAu_{2.2}Ga_{3.8}$ [6]		
Lattice parameters [pm]	a 491.53(3) b 803.68(5) c 954.79(6)	505.5(2) 800.1(4) 961.4(4)	516.3(1) 794.3(2) 959.7(2)	523.6(1) 785.4(2) 959.2(2)
$V_{u.c.}$ [10^6 pm ³]	377.17(4)	388.8(3)	393.52(14)	394.44(14)
R Value	R1 0.0787	0.0571	0.0385	0.0174

Table 2: Crystal data of selected In mercurides $RbHg_{6-x}In_x$.

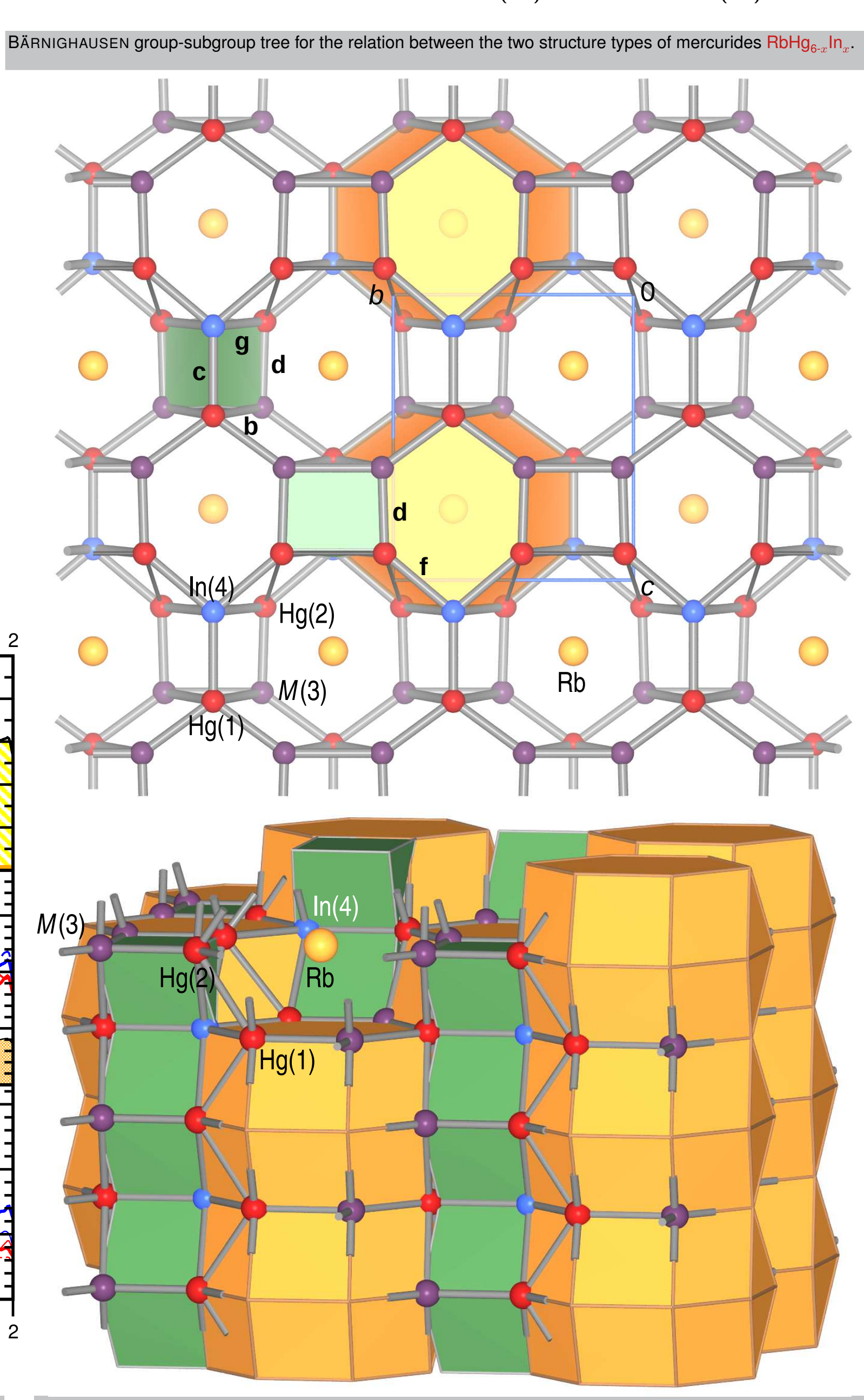
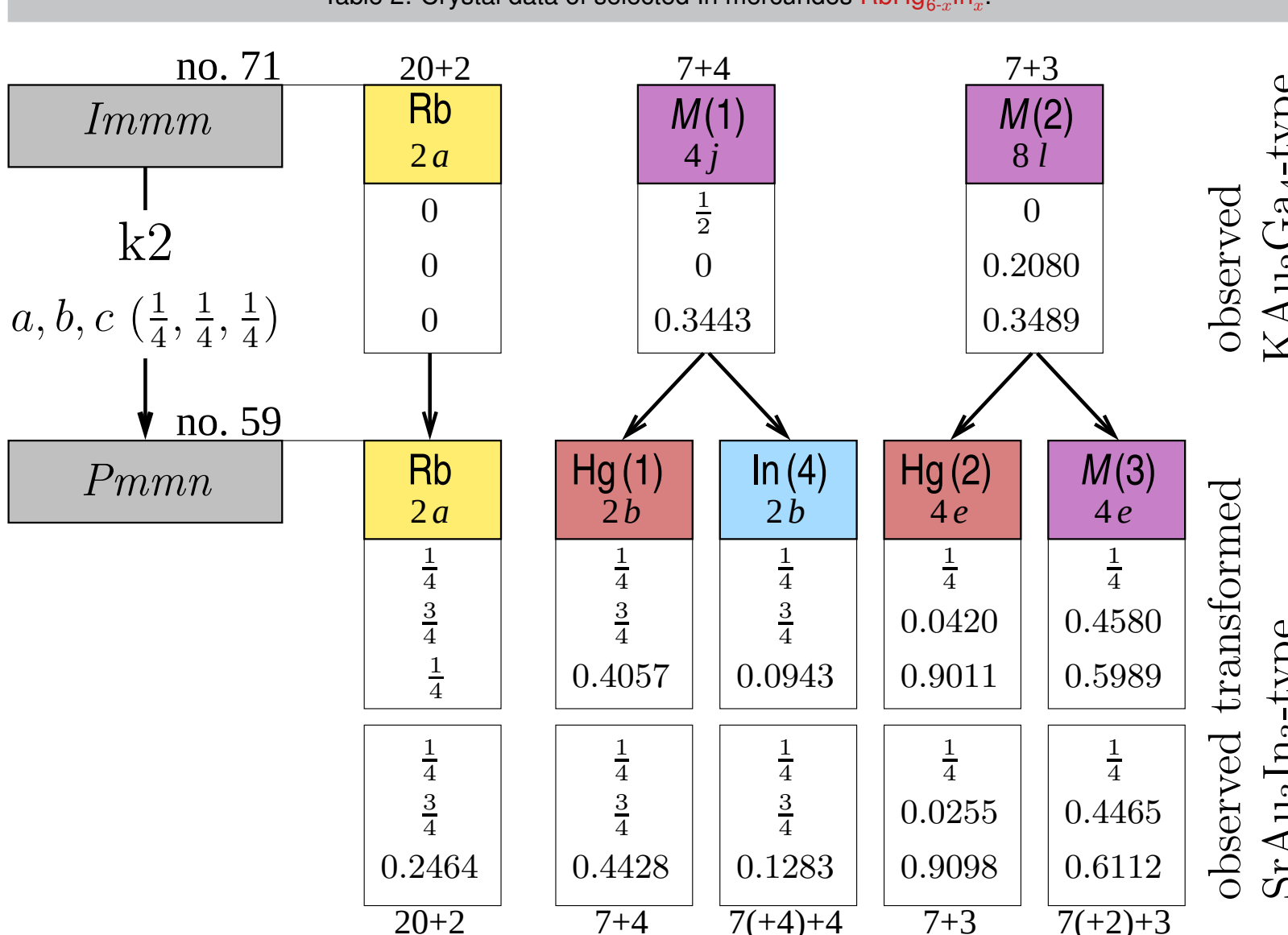


Fig. 6: Nets and packing aspect in the structure of $RbHg_{3.4}In_{2.6}$.

References and Experimental

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The ternary In-containing rubidium mercurides were synthesized from stoichiometric melts of the elements in Ta crucibles. The samples were heated with a rate of 200 K/h to a maximum temperature of 550 °C and were subsequently cooled to r.t. with a rate of 20 K/h. The compounds obtained from the different samples (SN) are indicated by gray arrows in Figure 1. The crystal structures have been determined by means of single crystal X-ray diffraction. For the smaller structures and (nearly) ordered Hg/In cases, DFT band structure calculations were performed using the FP-LAPW method (program WIEN2K, PBE-GGA functional).