A Coloring Study of the Ga Richest Alkali Gallides: New In- and Hg-Containing Gallides with the RbGa$_7$- and the K$_3$Ga$_{13}$-Type Structure

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Abstract: The Ga-rich gallides of the alkali metals present an interesting, yet still scarcely investigated case of polyanionic cluster compounds with subtle variations in the character of their chemical bonding. In the present work, the Ga richest phases K$_3$Ga$_{13}$, RbGa$_7$, and CsGa$_7$, which are formally electron-precise Zintl/Wade cluster compounds, are systematically studied with respect to a partial substitution of Ga by In and Hg. The pure hepta-gallides AGa$_7$ (A = Rb/Cs; R$\overline{3}$m), which were formerly obtained from Ga-rich melts in powder form only, were crystallized from Hg-rich melts. Herein, up to 9.9/13.6% (Rb/Cs) of Ga could be substituted by In, which partly takes the four-bonded $[M_2]$ dumbbells connecting layers of Ga-icosahedra. Even though the structures are electron precise, the pseudo band gap does not coincide with the Fermi level. In the most Ga-rich potassium compound K$_3$Ga$_{13}$ (Cmcm) only 1.2% of In and 2.7% of Hg could be incorporated. Although Rb$_3$Ga$_{13}$ remains unknown, ternary variants containing 5.2 to 8.2% In could be obtained; this structure is also stabilized by a small Hg-proportion. The likewise closed-shell 3D polyanion consists of all-exo-bonded Ga-icosahedra and closo $[Ga_{11}]$ clusters, which are connected by two tetrahedrally four-bonded Ga$^-$ and a trigonal-planar three-bonded Ga$^0$. The aspects of the electronic structures and the site-specific Ga$\rightarrow$Hg/In substitution in the polyanion (“coloring”) are discussed for the title compounds and other mixed Ga/In trielides.

Keywords: gallides; indium; mercury; alkali metals; cluster compounds; crystal growth; crystal structure; electronic structure

1. Introduction

Alkali ($A^1$) gallides form a large variety of fascinating complex structures associated with diverse chemical bonding features [1–4]. The Ga-rich phases are mostly electron-precise Zintl/Wade compounds with a covalently bonded electron-poor (v.e./Ga only slightly above three) gallide polyanion containing different types of closo clusters. For example, the structure of KGA$_3$ according to KGA$_3$ $\rightarrow$ $\frac{3}{2}$K$^+$ + [Ga$_3$]$^{2-}$ + Ga$^-$ contains dodecahedral clusters [Ga$_3$]$^{2-}$ connected via tetrahedrally bonded Ga$^-$ atoms [5,6]. Occasionally, the polyanions of those gallides even resemble the structures of elemental boron or B-rich borides (e.g., in the case of the title compound RbGa$_7$ [7]). The large number of chemically different triel (M) positions in their structures predestines this class of compounds for studies on the site preferences (“coloring”) of the different atom sites within the polyanions with element atoms differing in size, electronegativity, and even v.e. numbers. In addition to these closed-shell cluster compounds, simple intermetallics like, e.g., NaGa$_4$ (BaAl$_4$-type [8]) appear among
the alkali gallides as well. These compounds show no (pseudo) band gaps, as are typically associated with a larger variety of elements that may (partly) substitute gallium [9]. A puzzling bonding situation is also observed for the less triel-rich trielides like, e.g., Cs₈Ga₁₁ [10–12], which contain isolated clusters as anionic structure motifs.

The Ga richest gallides in the systems A–Ga of the three heavier alkali elements (A = K, Rb, Cs) are the starting point of the “coloring” study presented herein: RbGa₇ and CsGa₇ are the most electron-poor alkali metal trielides known (v.e./Ga = 3.143). They are still incompletely characterized to date, as the structure of RbGa₇ was solved and refined by Belin in 1981 [7] in the monoclinic subgroup C2/m of the correct trigonal space group R̅3m. This symmetry mistake was detected by Marsh [13], who suggested the transformation to the trigonal rhombohedral structure. These retroactively transformed data are recorded in the inorganic structure databases as final crystal data for RbGa₇ until today. In 1985, van Vucht [14] reported a refinement of the R̅3m structure model of the isotypic Cs compound CsGa₇ based on X-ray powder data. Unfortunately, this work lacks details of the parameter refinement procedure, which furthermore yielded implausible atomic displacement parameters. More recent structure refinements are not known, possibly due to the incongruent melting behavior of both compounds [15–19]. This behavior requires a huge excess of gallium for the crystal growth, the separation of which from the desired product is not straightforward (cf. the procedure described in [20]). The most Ga-rich potassium gallide is the yet singular orthorhombic phase K₃Ga₁₃ (v.e./Ga = 3.23). Its complex structure was conclusively solved by Belin forty years ago using single crystal four-circle diffractometer intensity data [20]. Both types of Ga-rich gallides belong to the family of electron-precise cluster compounds: In the polyanion of RbGa₇, [Ga₁₂]⁰ icosahedra are connected via [Ga₃] triangles (2e3c bonds) to form layers that resemble the structure of α-rhombohedral boron. The icosahedra layers are further connected via the dumbbells of four-bonded Ga⁻ atoms. K₃Ga₁₃ exhibits similar building blocks and is likewise a closed-shell compound: All-exo-connected icosahedra [Ga₁₂]⁻² and closo clusters [Ga₁₁]²⁻ (in a 1:1 ratio) are connected by two four-bonded Ga⁻ and one trigonal-planar bonded Ga⁰ atom.

The present work on the “coloring” [21] of the polyanions in the two Ga-rich gallides K₃Ga₁₃ and (Rb/Cs)Ga₇ with the larger In atoms extends our recent studies on mixed Ga/In trielides of the RbGa₇, Cs₂In₃ [22], BaAl₄ [9], and Cs₈Ga₁₁ [12] structure types. Due to the closed-shell character of the two gallides, the partial substitution of Ga by Hg, which differs not only in size and electronegativity, but in v.e. numbers as well, is initially not expected. The only hint towards this possibility is the Au-containing derivative of RbGa₃ reported by Henning and Corbett [23].

2. Experimental Section

2.1. Preparation and Phase Analysis

The synthesis of the title compounds was performed starting from the pure alkali metals, gallium and indium or mercury, as obtained from commercial sources (K, Rb, Cs: Metallhandelsgesellschaft Maassen, Bonn, 99%; Ga: ABCR Karlsruhe, 99.999%; In: rods, ABCR Karlsruhe, 99.99%; Hg: 99.9%, Merck KGaA). The elements were filled into tantalum crucibles in a glovebox under an argon atmosphere, and the welded containers were heated up with a rate of 200 °C⁻¹ to maximum temperatures between 370 and 700 °C. For all samples, the crystallization was performed applying a slow cooling rate of 2 to 10 °C⁻¹. The temperature programs applied can be found in Table 1, together with the weighed sample compositions and the results of the X-ray powder diffraction data. For the latter, representative parts of the reguli were ground and sealed in capillaries with a diameter of 0.3 mm. X-ray powder diagrams were collected on transmission powder diffraction systems (STADI-P, Dectris Mythen 1K detector, Stoe & Cie, Darmstadt, MoKα₁ radiation). For the phase analysis, the measured diffraction data were compared to the calculated (program LAZY-PULVERIX [24]) reflections of the title compound and other known phases in the ternary system K/Rb/Cs–Ga–In/Hg.
Table 1. Details of the synthesis of Ga-rich alkali gallides (tr: traces, s.c.: single crystals, * full s.c. dataset; cf. Tables 2 and 6).

| No. | Composition | K/Rb/Cs | Weighed Elements | Temperature Program | Products, as Identified from Powder and Single Crystal (*) Data |
|-----|-------------|---------|------------------|---------------------|-------------------------------------------------------------|
|     |             | /mg     | Ga   | In/Hg | $T_{max}$ | $T_{up}$ | $T_{down}$ | $T_{final}$ |
| K1a | $K_3Ga_{1.5}In_{2.5}$ | 89 | 2.27 | 345 | 4.94 | 567 | 4.94 | 500 | 10 |
| K1b | $K_3Ga_{2}In_{3}$ | 90 | 2.28 | 344 | 4.94 | 567 | 4.94 | 700 | 50 |
| K2  | $K_2Ga_{1.5}In_{3}$ | 101 | 2.59 | 602 | 8.63 | 297 | 2.59 | 500 | 10 |
| K3  | $K_3Ga_{1}In_{2}$ | 105 | 2.69 | 689 | 9.88 | 207 | 1.80 | 700 | 50 |
| K4  | $K_3Ga_{1.5}In_{1.5}$ | 108 | 2.75 | 735 | 10.54 | 157 | 1.37 | 500 | 10 |
| K5  | $K_3Ga_{2}In_{5}$ | 32 | 0.83 | 809 | 11.60 | 159 | 1.38 | 700 | 5 |
| K6  | $K_3Ga_{3}Hg_{3}$ | 91 | 2.33 | 484 | 6.94 | 1392 | 6.94 | 700 | 20 |
| K7  | $K_3GaHg_{3}$ | 114 | 2.92 | 201 | 2.88 | 1726 | 8.60 | 700 | 20 |
| Rb1 | $RbGa_{1.5}In_{2.5}$ | 127 | 1.48 | 458 | 6.56 | 419 | 3.65 | 650 | 5 |
| Rb2 | $RbGa_{1}In$ | 141 | 1.64 | 676 | 9.70 | 186 | 1.62 | 650 | 5 |
| Rb3 | $RbGa_{1.5}In_{1.5}$ | 62 | 0.73 | 530 | 7.60 | 409 | 3.56 | 550 | 3 |
| Rb4 | $RbGa_{1}In_{1.5}$ | 67 | 0.76 | 647 | 9.28 | 229 | 2.51 | 370 | 3 |
| Rb5a| $RbGa_{2}In_{3}$ | 71 | 0.83 | 779 | 11.17 | 153 | 1.33 | 550 | 3 |
| Rb5b| $RbGa_{1}In_{1.5}$ | 71 | 0.83 | 779 | 11.17 | 153 | 1.33 | 550 | 3 |
| Rb5c| $RbGa_{1}In_{1.5}$ | 69 | 0.81 | 779 | 11.17 | 151 | 1.32 | 370 | 3 |
| Rb6 | $RbGa_{1}In_{1.5}$ | 123 | 1.44 | 148 | 2.12 | 731 | 6.37 | 370 | 3 |
| Rb7 | $RbGa_{3}Hg_{3}$ | 170 | 1.99 | 497 | 7.13 | 1427 | 7.11 | 700 | 20 |
| Rb8 | $RbGaHg_{3}$ | 246 | 2.88 | 187 | 2.68 | 1608 | 8.02 | 650 | 50 |
| Cs1 | $CsGa_{3}In_{3}$ | 104 | 0.77 | 751 | 10.8 | 148 | 1.28 | 550 | 5 |
| Cs2 | $CsGa_{1}In_{1.5}$ | 97 | 0.73 | 624 | 8.97 | 278 | 2.42 | 550 | 5 |
| Cs3 | $CsGa_{1.5}In_{1.5}$ | 137 | 1.04 | 326 | 4.67 | 536 | 4.67 | 550 | 5 |
| Cs4 | $CsGaHg_{3}$ | 345 | 2.60 | 173 | 2.48 | 1500 | 7.48 | 700 | 20 |
In the ternary system K–Ga–In, indium richer samples at the pseudo-binary section A$_3$M$_{13}$ (e.g., samples K1 and K2; Table 1) yielded members of the recently newly obtained orthorhombic A$_2$M$_{11}$ phases K$_x$Ga$_{31-x}$In$_x$ ($x = 1.16 - 1.36$, [25]) if the maximum temperature was kept at 500 °C. At a reduced In content, i.e., below a Ga:In ratio of 11:2 (samples K3 and K4), variable amounts (depending on the temperature program) of the A$_2$M$_{11}$ trielides (for T$_{\text{max}} = 500$ °C) and ternary In-substituted derivative of the K$_3$Ga$_{13}$-type (T$_{\text{max}} = 700$ °C) are formed. As the binary gallide K$_7$Ga$_3$ [20] is known to melt incongruently and the peritectic line at 510 °C meets the liquidus curve at approximately 6% K [18,29], well-developed needle-shaped crystals of the most In-rich K$_3$Ga$_{13}$-type phase were obtained from the triel-rich sample K$_3$Ga$_{42}$In$_5$ (K5), again at a maximum temperature of 700 °C. By-products were In-substituted KGa$_3$-type phases [5,22] and elemental gallium. Attempts to crystallize the incongruently melting Ga-rich gallides from liquid mercury in samples of overall composition KGa$_3$Hg$_3$ (K6) and KGaHg$_3$ (K7) yielded—together with KHg$_6$ [26] and K$_2$Hg$_7$ [27], respectively—nice needle-shaped crystals of the ternary Hg-containing derivative K$_2$Ga$_{12.65}$Hg$_{0.35}$ of the K$_3$Ga$_{13}$-type.

In the corresponding rubidium system Rb–Ga–In, an analogous border phase Rb$_2$Ga$_{13}$ is unknown. Here, RbGa$_7$ [7,13] is the most Ga-rich compound of the binary system Rb–Ga [15–17]. This compound, similar to K$_3$Ga$_{13}$, exhibits incongruent melting behavior, with a peritectic temperature of 354 °C. The phase diagram substantiates that the growth of the crystals of this compound is only possible from very Ga-rich samples with a Rb content of less than 1%. As the structures of the RbGa$_7$-type do not take up mercury, the crystallization of well-developed crystals of RbGa$_7$ was possible from a sample RbGa$_{35.5}$In$_{3.3}$ (Rb7; cf. Table 1). An increased amount of rubidium (Rb:Ga = 1:1, sample RbGa$_{12}$Hg$_3$, Rb8) yielded the Rb-analog compound Rb$_3$Ga$_{12.58}$Hg$_{0.42}$ of the K$_3$Ga$_{13}$-type (together with the byproduct Rb$_2$Hg$_{16}$), even though the pure gallide Rb$_3$Ga$_{13}$ is unknown. Likewise, several In-substituted derivatives of this unknown gallide and of RbGa$_7$ could be obtained, again from triel-rich samples. In accordance with the incongruent melting of both types of compounds, samples with an overall composition AM$_7$ (i.e., 12.5% Rb; Rb1 and Rb2) yielded crystals of ternary KGa$_3$-type derivatives only [22]. At a reduced Rb content of 6% (A$_3$M$_{17}$) and for In poorer samples [Rb$_3$Ga$_{42}$In$_{15}$ (Rb3) still contained KGa$_3$-type compounds besides elemental In], i.e., from the samples Rb4 (Rb$_3$Ga$_{37}$In$_{10}$) and Rb5a-c (Rb$_3$Ga$_{42}$In$_9$), ternary In-derivatives of RbGa$_7$ and the K$_3$Ga$_{13}$-type structure could be obtained. The In-rich sample RbGa$_{15}$In$_{4.5}$ (Rb4) resulted in the formation of the most In-rich derivative of the RbGa$_{13}$-type compounds, RbGa$_{8.31}$In$_{0.69}$, in addition to RbIn$_3$ and an excess of elemental In.

The only known binary Ga-rich Cs-gallide is CsGa$_7$ [18]. Its peritectic isothermal line at 426 °C intersects the liquidus curve at approximately 3% Cs [15,18,19], which again allows the single crystal growth only in the presence of a large excess of gallium. Similar to RbGa$_7$, described above, well-developed crystals of CsGa$_7$ could be obtained from a melt of mercury (sample Cs4: CsGaHg$_3$). Indium substituted derivatives of CsGa$_7$, with an In content of up to 9%, were again obtained from the samples Cs$_3$M$_{17}$ (Cs1 and Cs2). The most In-rich phase (13.6% In) was yielded—together with a ternary variant of the KGa$_3$-type trielides and elemental In—from the sample CsGa$_{4.5}$In$_{4.5}$ (Cs3).

2.2. Crystal Structure Refinements

The silver-metallic crystals of the title compounds were fixed under dried paraffin oil in glass capillaries (⌀ < 0.1 mm) and centered on a diffractometer equipped with a sealed tube and an image plate detector (Stoe IPDS-2) or a micro-source-equipped CCD detector (Apex Quazar).
The reflections of the plate-like crystals of the binary gallides RbGa\textsubscript{7} and CsGa\textsubscript{7}, which were obtained from Hg-melts in the samples Rb\textsubscript{7} and Cs\textsubscript{4} (cf. * in Table 1), could be indexed using the expected trigonal rhombohedral unit cell. The refined unit cell parameters (Table 2) are in very good agreement with the transformed values of Belin for the Rb phase (\(a = 660.3(2), c = 2856.6(3)\) pm [7]) and with the powder data obtained by van Vucht for the Cs gallide (\(a = 662.0(1), c = 2904.5(1)\) pm [14]).

The collected single crystal data show no additional extinction conditions, and the symmetry of the intensities corresponds to the high Laue class, both fitting the expected space group \(R\overline{3}m\). The refinement of the (standardized and transformed, program S\textsc{TRUCTURE}T\textsc{IDY} [30]) atomic coordinates of the structure model published by Belin [7] smoothly converged to low residual values \(R_1\) below 3\% (program S\textsc{HELXL}-2013 [31]; cf. Tables 2 and 3). The data for the isotypic mixed Ga/In trielides with the maximum indium proportions were collected using crystals obtained from the In richer samples Rb\textsubscript{6} and Cs\textsubscript{3}. In agreement with the incorporation of the larger indium atoms, the lattice parameters are slightly (approximately 1\%) increased with respect to the pure gallides. During the structure refinement, the Ga(3) position turned out to remain a pure gallium site. The Ga(2) position, which forms the icosahedra together with Ga(3), contains only very small amounts of indium. The four-bonded \(M(1)\) position shows the highest In-proportions of up to 80\% in the Cs compound. The final structure refinements, the two statistically occupied positions \(M(1)\) and \(M(2)\) were treated using constrained positional and thermal parameters. The overall compositions for the two In richest border phases are finally RbGa\textsubscript{6.31}In\textsubscript{0.69} (9.9\% In) and CsGa\textsubscript{6.05}In\textsubscript{0.95} (13.6\% In). The crystal data of the four RbGa\textsubscript{7}-type compounds are collected in Tables 2 and 3; selected interatomic distances are listed in Table 4 [32].

Table 2. Crystallographic data and details of the data collection and structure refinement of the RbGa\textsubscript{7}-type gallides.

| Compound | RbGa\textsubscript{7} \(\text{In/Hg content %}\) | RbGa\textsubscript{6.31}In\textsubscript{0.69} | CsGa\textsubscript{7} | CsGa\textsubscript{6.05}In\textsubscript{0.95} |
|----------|--------------------------------|------------------|-----------------|------------------|
| In/Hg content % | 0 | 9.9(2) | 0 | 13.6(4) |
| Structure type, Pearson symbol | RbGa\textsubscript{7} [7], \(\text{trR48}\) | RbGa\textsubscript{7} [7], \(\text{trR48}\) | | |
| Crystal system, space group | trigonal, \(R\overline{3}m\), No. 166 | | | |
| Lattice parameters, pm | \(a = 661.1(2)\) | \(662.96(3)\) | \(661.76(8)\) | \(668.46(2)\) |
| | \(c = 2860.5(8)\) | \(2887.1(2)\) | \(2904.1(3)\) | \(2961.16(14)\) |
| Volume of the u.c., 10\textsuperscript{6} pm\textsuperscript{3} | 1082.7(7) | 1098.94(11) | 1101.4(3) | 1145.89(9) |
| \(Z\) | 6 | | | |
| Density (X-ray), gcm\textsuperscript{-3} | 5.28 | 5.48 | 5.62 | 5.77 |
| Diffractometer | APEX | IPDS | APEX | IPDS |
| Radiation | Mo-K\textsubscript{α} | Ag-K\textsubscript{α} | Mo-K\textsubscript{α} | Ag-K\textsubscript{α} |
| Absorption coeff. \(\mu\text{Mo/Ag-K\textsubscript{α}}\) \text{\textsuperscript{-1}}/\text{mm\textsuperscript{-1}} | 32.31 | 16.60 | 10.02 | 14.93 |
| `range, deg. | 2.1–30.1 | 1.7–27.9 | 2.1–30.0 | 1.6–26.8 |
| No. of reflections collected | 8957 | 12,875 | 6396 | 12,050 |
| No. of independent reflections | 452 | 725 | 454 | 675 |
| \(R_{int}\) | 0.0733 | 0.0491 | 0.0525 | 0.0473 |
| Corrections | | | | |
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Table 3. Atomic coordinates and equivalent isotropic displacement parameters/pm$^2$ for the crystal structures of the RbGa$_7$-type gallides.

| Atom | Wyckoff Position | Parameter | RbGa$_7$ | RbGa$_{6.31}$In$_{0.69}$ | CsGa$_7$ | CsGa$_{6.05}$In$_{0.95}$ |
|------|------------------|-----------|-----------|--------------------------|-----------|--------------------------|
| A    | 6c 0,0,z         | z         | 0.30521(3) | 0.30501(4) | 0.30662(2) | 0.30623(2) |
| M(1) | 6c 0,0,z         | U$_{\text{equiv.}}$ | 285(3) | 247(3) | 232(2) | 222(2) |
| M(2) | 18h x,−x,z      | z         | 0.04418(4) | 0.04480(3) | 0.04448(4) | 0.04630(3) |
|      |                  | U$_{\text{equiv.}}$ | 189(3) | 179(3) | 222(2) | 183(3) |
|      |                  | In content % | 0 | 40(2) | 0 | 792(2) |
| Ga(3) | 18h x,−x,z | x | 0.47309(6) | 0.47145(6) | 0.47370(6) | 0.46941(6) |
|      |                  | z | 0.14785(2) | 0.14828(2) | 0.14812(2) | 0.14897(2) |
|      |                  | U$_{\text{equiv.}}$ | 205(2) | 190(2) | 199(2) | 221(2) |

Table 4. Selected interatomic distances/pm in the crystal structures of the compounds forming the RbGa$_7$-type structure.

| Atoms | Distance in Label Freq. | CN |
|-------|-------------------------|----|
| A     | -M(2) 372.5(1)          | 3× |
|       | -Ga(3) 374.4(1)         | 3× |
|       | -M(2) 375.5(1)          | 6× |
|       | -M(1) 384.4(1)          | 3× |
|       | -A 414.2(1)             | 3× |
|       | -M(1) 434.1(1)          | 3× |
|       | M(1) -A 256.8(1)        | 3× |
| M(1)  | -M(1) 252.7(2)          | a  |
|       | -M(2) 256.8(1)          | b  |
|       | -A 384.4(1)             | 3× |
|       | -A 434.1(1)             | 3× |
|       | M(2) -A 256.8(1)        | 3× |
|       | -Ga(3) 263.9(1)         | c  |
|       | -M(2) 277.2(1)          | d  |
|       | -Ga(3) 283.5(1)         | e  |
|       | -A 372.5(1)             | 2× |
|       | -A 375.5(1)             | 2× |
| Ga(3) | -Ga(3) 254.3(1)         | f  |
|       | -Ga(3) 262.2(2)         | g  |
|       | -M(2) 263.9(1)          | c  |
|       | -M(2) 283.5(1)          | e  |
|       | -A 374.4(1)             | 7× |

Needle-shaped crystals of the ternary In- and Hg-containing derivatives of K$_3$Ga$_{13}$ were obtained from the samples K$_5$ and K$_7$. Their diffraction images exhibit the expected orthorhombic symmetry with extinction conditions compatible with the space group of this structure type (Cmcm). The lattice parameters, mainly the length of the b axis, are slightly enlarged with respect to the values of K$_3$Ga$_{13}$ itself (a = 644.1(3), b = 1614.3(3), c = 2840.4(7) pm [20]). The structure model of K$_3$Ga$_{13}$, which contains eleven Ga and three K sites, was used for the refinement of the structures, and all gallium sites were checked for a possible mixed Ga/In or Ga/Hg occupation. In the case of the In gallides, the cluster site M(11) exhibits the largest substitution. In contrast, the likewise larger Hg atoms are incorporated at the three-bonded position M(1) exclusively. Although the indium and mercury content of the samples K$_5$ and K$_7$ was much higher, the final resulting compositions K$_3$Ga$_{12.85}$In$_{0.15}$ (1.2% In) and
K$_3$Ga$_{12.65}$Hg$_{0.35}$ (2.7% Hg) indicate only a small substitution of gallium by the larger atoms In and Hg. Ternary In and Hg containing derivatives of the unknown gallide Rb$_3$Ga$_{13}$ were obtained from the samples Rb$_4$, Rb$_5$a, and Rb$_8$. Here, the proportion of larger M atoms is increased compared to the potassium phases, but the site preferences (In mainly at M(11), Hg at M(1)) are nevertheless similar. The phase width $x$ of the In-derivatives Rb$_3$Ga$_{13-x}$In$_x$ reaches from $x = 0.68$ to $1.07$; the Hg content in Rb$_3$Ga$_{13-x}$Hg$_x$ is $x = 0.42$. The atomic parameters are given in Table 5 [32], and Table 6 contains the crystal data of the new ternary members of the K$_3$Ga$_{13}$-type.

2.3. Band Structure Calculations

DFT calculations of the electronic band structure were performed for the three binary gallides RbGa$_7$, CsGa$_7$, and K$_3$Ga$_{13}$ and the two model compounds “CsGa$_6$In” (M(1) fully occupied by In; crystal data taken from CsGa$_{6.05}$In$_{0.95}$, Tables 2 and 3) and “Rb$_6$Ga$_{25}$Hg” (M(1) fully occupied by Hg; data from Rb$_3$Ga$_{12.58}$Hg$_{0.42}$, Tables 5 and 6). α-rhombohedral boron (for the data, cf. [35]) was calculated likewise for comparison. In the FP-LAPW (Full-Potential Linear Augmented Plane Wave) method implemented in the program WIEN2k [36], the exchange-correlation contribution is described by the Generalized Gradient Approximation (GGA) of Perdew, Burke, and Ernzerhof [37]. Muffin-tin radii were chosen as 121.7 pm (2.3 a.u.) for all heavy atoms and 79.4 pm (1.5 a.u.) for boron. The cutoff energies used are $E_{\text{pot}}^{\text{max}} = 190$ eV (potential) and $E_{\text{wf}}^{\text{max}} = 170$ eV (interstitial PW). The calculations were carried out on a Monkhorst–Pack grid of 21×21×21 (for the small primitive unit cells of RbGa$_7$-type/α-rhom. B) and 16×16×3 for the larger orthorhombic K$_3$Ga$_{13}$-type compounds (cf. Table 9 for further details). Electron densities and Fermi surfaces were calculated and visualized using the programs XCrySDen [38] and DRAWXTL [39]. Bader AIM analyses of the electron density maps were performed to evaluate the charge distribution between the atoms and the heights and positions of the bond, ring, and cage critical points [40] using the program CRITIC2 [41,42]. Selected results of these analyses (Bader volumes and charges) are summarized in Table 9. The total (tDOS) and some selected partial densities of state (pDOS) are depicted in Figure 3 (CsGa$_7$ and CsGa$_6$In) and Figure 4 (K$_3$Ga$_{13}$). The band structure and key energy-selected valence electron densities of CsGa$_7$ and α-rhombohedral boron can be found in Figure 5.

### Table 5. Atomic coordinates and equivalent isotropic displacement parameters/pm$^2$ for the crystal structures of the ternary gallides forming the K$_3$Ga$_{13}$-type structure.

| Atom | Wyckoff Position | Parameter | K$_3$Ga$_{12.85}$In$_{0.15}$ | K$_3$Ga$_{12.65}$Hg$_{0.35}$ | Rb$_3$Ga$_{12.32}$In$_{0.68}$ | Rb$_3$Ga$_{11.93}$In$_{1.07}$ | Rb$_3$Ga$_{12.58}$Hg$_{0.42}$ |
|------|------------------|-----------|-----------------------------|-----------------------------|--------------------------------|--------------------------------|--------------------------------|
| A(1) 0, y, z 8f | $y$ 0.13795(12) $z$ 0.67963(9) | $U_{\text{equiv.}}$ 383(5) $U_{\text{equiv.}}$ 260(3) | 0.13783(7) 0.68175(6) | 0.13645(12) 0.67918(8) | 0.13671(11) 0.67911(8) | 0.13737(3) 0.68110(2) | 0.331.4(14) 0.58732(2) |
| A(2) 0, y, z 8f | $y$ 0.28682(10) $z$ 0.58520(7) | $U_{\text{equiv.}}$ 260(3) $U_{\text{equiv.}}$ 263(3) | 0.28712(7) 0.58578(4) | 0.28734(11) 0.58676(6) | 0.28720(10) 0.58600(6) | 0.28777(3) 0.58732(2) | 0.253.9(12) 0.58732(2) |
| A(3) 0, y, z 8f | $y$ 0.48479(12) $z$ 0.13881(6) | $U_{\text{equiv.}}$ 260(3) $U_{\text{equiv.}}$ 263(3) | 0.48475(8) 0.14082(4) | 0.48312(13) 0.13938(6) | 0.48414(12) 0.13920(6) | 0.48259(4) 0.14143(2) | 0.268.4(12) 0.4177(2) |
| M(1) 0, y, 1/4 4c | $y$ 0.42740(7) | $U_{\text{equiv.}}$ 197(4) $U_{\text{equiv.}}$ 263(3) | 0.42126(2) 0.14082(4) | 0.43336(19) 0.13938(6) | 0.43480(18) 0.13920(6) | 0.42177(2) 0.14143(2) | 0.42177(2) 0.14143(2) |

In/Hg content % 8(1) 70.2(3) 9(3) 11(3) 11(3) 84.2(3)
Table 5. Cont.

| Atom | Wyckoff Position | Parameter | Compounds |
|------|------------------|-----------|-----------|
| M(2) | 0, y, z          | y         | K₃Ga₁₂,₃In₉,₁₅ |
|      | 8f               | z         | K₃Ga₁₂,₃Hg₉,₃₅ |
|      |                  |           | R₆₂Ga₁₂,₃In₉,₁₅ |
|      | In content %     | 0         | 0.29859(5) |
|      |                  |           | 0.29712(3) |
|      |                  |           | 0.299071(11) |
|      |                  |           | 0.29951(10) |
|      | In equiv.        | 156(2)    | 183.7(11) |
|      |                  |           | 286(6) |
|      |                  |           | 221(6) |
|      |                  |           | 190.8(12) |
| M(11)| 0, y, 1/4        | y         | 0.27368(6) |
|      |                  |           | 0.26919(5) |
|      |                  |           | 0.27782(15) |
|      |                  |           | 0.27812(13) |
|      |                  |           | 0.26952(5) |
|      | In content %     | 0         | 21.3(14) |
|      |                  |           | 0         |
| M(12)| 0, y, z          | y         | 0.24087(6) |
|      |                  |           | 0.24034(3) |
|      |                  |           | 0.23987(14) |
|      |                  |           | 0.23945(12) |
|      |                  |           | 0.23994(4) |
|      | In content %     | 206(2)    | 230.1(12) |
|      |                  |           | 328(7) |
|      |                  |           | 248(7) |
|      |                  |           | 221.2(13) |
| Ga(13)| 0, y, z          | y         | 0.07324(5) |
|      |                  |           | 0.07268(3) |
|      |                  |           | 0.07614(13) |
|      |                  |           | 0.07567(12) |
|      |                  |           | 0.07468(4) |
|      | In content %     | 166(2)    | 196.5(11) |
|      |                  |           | 276(4) |
|      |                  |           | 198(4) |
|      |                  |           | 197.9(12) |
| Ga(14)| x, y, 1/4       | x         | 0.20858(13) |
|      |                  |           | 0.21106(8) |
|      |                  |           | 0.2067(3) |
|      |                  |           | 0.2058(3) |
|      |                  |           | 0.21094(9) |
|      | In content %     | 162(2)    | 155.98(13) |
|      |                  |           | 170.79(6) |
|      |                  |           | 170.85(7) |
|      |                  |           | 171.19(2) |
| Ga(15)| x, y, z          | x         | 0.20307(2) |
|      |                  |           | 0.20534(2) |
|      |                  |           | 0.20351(4) |
|      |                  |           | 0.20348(5) |
|      |                  |           | 204.05(2) |
|      | In content %     | 172.4(12)| 193.81(3) |
|      |                  |           | 170.81(3) |
|      |                  |           | 170.79(7) |
|      |                  |           | 171.02(3) |
| M(21)| 0, y, z          | y         | 0.15655(5) |
|      |                  |           | 0.15598(3) |
|      |                  |           | 0.15621(12) |
|      |                  |           | 0.15574(11) |
|      |                  |           | 0.15602(3) |
|      | In content %     | 158(2)    | 193.3(11) |
|      |                  |           | 287(6) |
|      |                  |           | 248(7) |
|      |                  |           | 196.3(12) |
| Ga(22)| 0, y, z          | y         | 0.01576(5) |
|      |                  |           | 0.01476(3) |
|      |                  |           | 0.01861(13) |
|      |                  |           | 0.01893(12) |
|      | In content %     | 157(2)    | 170.81(3) |
|      |                  |           | 170.79(7) |
|      |                  |           | 171.02(3) |
| Ga(23)| x, y, z          | x         | 0.29649(8) |
|      |                  |           | 0.29421(5) |
|      |                  |           | 0.2977(2) |
|      |                  |           | 0.2985(2) |
|      | In content %     | 152.8(11)| 182.19(9) |
|      |                  |           | 273(3) |
|      |                  |           | 196(3) |
|      |                  |           | 187.3(9) |
| Ga(24)| x, y, z          | x         | 0.30718(8) |
|      |                  |           | 0.30599(5) |
|      |                  |           | 0.30700(19)|
|      |                  |           | 0.3074(2) |
|      | In content %     | 140.4(11)| 169.5(9) |
|      |                  |           | 256(3) |
|      |                  |           | 175(3) |
|      |                  |           | 173.8(9) |

3. Results and Discussion

3.1. Synthesis, Crystal Growth, and Phase Widths

The most Ga-rich alkali gallides RbGa₇ [7, 13] and CsGa₇ [18] both exhibit a peritectic melting behavior. As their peritectic lines at 354/426 °C (for A = Rb/Cs) meet the liquidus curves at very low A proportions (<3% [15, 18, 19]), single crystal growth of these compounds requires a large excess of gallium. Due to the lack of a suitable position in the structure of the RbGa₇-type, these compounds—in contrast to the A₃M₄₇ phases (see below)—do not take up any mercury, and the crystallization of well-developed plate-shaped crystals of both hepta-gallides was possible from Hg-rich melts applying slow cooling rates of 2 °C/h (samples RbGa₃.₅Hg₃.₅ (Rb₇), and CsGaHg₃ (Cs₄); cf. Table 1). Similarly, indium-substituted derivatives A₃Ga₇-xInₙ of RbGa₇ and CsGa₇ were obtained from triel-rich samples of overall composition A₃M₄₇, inevitably with elemental Ga or In as byproducts. The most In-rich phases of this structure type, which contain x = 0.69/0.95 In and represent the border compositions of the phase width x, were still yielded from the A₃ and In richer samples RbGa₁.₅In₄.₅ and CsGa₄.₅In₄.₅, in these cases with elemental indium and ternary BaAl₄- and KGa₃-type trielides as by-products.
Similar to RbGa$_7$ and CsGa$_7$, the most Ga-rich gallide of the K–Ga system, K$_3$Ga$_{13}$ [20] also melts incongruously at 510 °C. Here, the liquidus curve is touched at approximately 6% K [18,29]. In accordance, needle-shaped single crystals of the most In-rich ternary K$_3$Ga$_{13}$-type phase, which however contains only 1.2% of In, were obtained from the triel-rich samples with the appropriate A content, like, e.g., K$_3$Ga$_{12}$In$_7$, applying slow cooling rates. The latter K-poor sample also proves the lack of mixed AM$_7$ phases for the alkali element potassium. Although the analog binary gallide Rb$_3$Ga$_{13}$ is unknown, In-containing ternary phases of the K$_3$Ga$_{13}$-type structure, within the small composition range $x_1 = 0.69$ to $x_2 = 1.07$ (for Rb$_3$Ga$_{13}$, In$_x$), were yielded from triel-rich samples Rb$_3$M$_{47}$ of variable In proportions ($x_1$: sample Rb$_3$Ga$_{42}$In$_9$, Rb$_5$a; $x_2$: sample Rb$_3$Ga$_{23}$In$_{10}$, Rb$_4$).

Additionally, attempts to crystallize the incongruently melting potassium and rubidium gallides (which were initially obtained as by-products of our work on mixed Hg/triel intermetallics [43]) from liquid mercury yielded (together with the Hg-rich potassium mercurides like KHg$_{56}$, K$_2$Hg$_7$ and Rb$_2$Hg$_{19}$) the ternary Hg-containing K$_3$Ga$_{13}$-type derivatives K$_3$Ga$_{12.65}$Hg$_{0.35}$ (from samples of as diverse compositions as KGaHg$_3$, and K$_2$Ga$_2$Hg$_5$) and Rb$_3$Ga$_{12.58}$Hg$_{0.42}$ (from the sample RbGaHg$_{53}$, Rb$_8$). As described above, an increased Ga:Rb ratio (sample RbGa$_3$H$_{83}$, Rb$_7$) favors the formation of the Ga-rich gallide RbGa$_7$.

### 3.2. Crystal Structure Descriptions

In accordance with the high Ga content and the large electronegativity of gallium, the RbGa$_7$-type structure [7] shows distinct structural similarities with the a-rhombohedral allotrope of boron: analogous to the structure of a-rhombohedral boron, the two binary hepta-gallides AGa$_7$ (A = Rb, Cs) and their slightly In-substituted derivatives contain hexagonal close-packed layers of empty close [Ga(2,3)$_{12}$] icosahedra (green polyhedra in Figure 1). Within these layers, the icosahedra (point group 3m) are condensed via [Ga(3)$_3$] triangles (magenta planes in Figure 1c). In contrast to the structure of a-boron, where the icosahedra of adjacent layers are directly connected via exo-bonds, the [Ga$_{12}$] icosahedra in AGa$_7$ are further connected via dumbbells of four-bonded M(1) atoms to form a three-dimensional network. According to the likewise rhombohedral symmetry, the icosahedra stacking sequence along [001] is :ABC:$. Compared to an ideal cubic close packing, the intra-layer distances between the icosahedra (cf. the lengths of the a axes of 660-670 pm) are much smaller than the inter-layer distances (1026 pm for RbGa$_7$). This is evidently a consequence of the [M(1)$_2$] dumbbells, which occupy the octahedral voids of the icosahedra packing. The shortest interatomic Ga–Ga distances a of 252.7/258.3 pm (for RbGa$_7$/CsGa$_7$) are found within these dumbbells, which are formed by the four-bonded Ga(1) atoms (Table 4).

Due to the preferred indium substitution of this site (cf. the “coloring” discussion in Section 3.4), this bond length increases significantly with the increasing In proportion of M(1). Nevertheless, with respect to the high In substitution of 80% in CsGa$_{6.05}$In$_{0.95}$, the M(1)–M(1) distance of 275.4 pm still represents a short and strong bond. The bonds b, which connect the dumbbells with the icosahedra, are also considerably short and lengthen similarly with the In content of the M(1) position. The endohedral bonds within the [Ga$_{12}$] icosahedra (c-f) vary between 254.3/255.6 and 283.5/282.9 pm for the two binary gallides. Due to the only very minimal substitution of the cluster-forming position M(2) (and the always pure gallium site Ga(3)), these distances are mainly unchanged in the two ternary mixed derivatives. Remarkably, the endohedral bond f is much shorter than the three other distances within the cluster, so that the icosahedra are slightly “stretched” along the crystallographic three-fold axis. The Ga(3)–Ga(3) distances within the connecting [Ga(3)$_3$] triangles (g: 262.4–264.6 pm for all four compounds) are also in the range of the intra-cluster values (cf. The discussion of the electronic structure and the comparison with the related a-rhombohedral boron structure in Section 3.3).
The Rb/Cs cations (Wyckoff position 6c: 3m symmetry) take the elongated tetrahedral voids of the icosahedra packing, which is apparent from the four icosahedra arranged around the yellow cation coordination polyhedron (CCP) in Figure 1b. According to the subdivided doubled formula:

\[
\text{Rb}_2 \left[ \left( \text{Ga(1)} \right)_2 \right] \left( \left[ \text{Ga(2,3)} \right]_{12} \right)_{\text{ABC}}
\]

the dense icosahedra packing provides one octahedral ([Ga\(_3\)] dumbbell) and two tetrahedral voids (Rb) per sphere/icosahedron. The coordination sphere of the alkali cations thus consists of 15(+3) \(M\) anion atoms (Table 4), of which \(4 \times 3\) are the [Ga\(_3\)] faces of the four adjacent icosahedra and \(3(+3)\) are the \(M(1)\) atoms of the three surrounding dumbbells (Figure 1b). The Rb–\(M\) distances vary from 372 to 385 pm (+ 3\(\times\) \(M\) at \(\approx\) 440 pm). As expected, the corresponding values in the Cs compounds are at 377 to 418 pm (again + 3\(\times\) \(\approx\) 440 pm) somewhat larger (Table 4). The shortest \(A\)–\(A\) distances are 414 to 418 pm (3\(\times\) ), and the Rb/Cs cations form As-analog layers among each other, which are of course stacked along \(c\) similar to As in rhombohedral \(\alpha\)-arsenic.
The orthorhombic structure of the K₃Ga₁₃-type consists of a three-dimensional network of two crystallographically different empty closo clusters, [M₁₂] icosahedra (green polyhedra in Figure 2), and [M₁₁] clusters (blue polyhedra), which are connected among each other and with two additional M atoms M(1) and M(2) via 2e2c bonds.

The [M₁₂] icosahedra are located around the Wyckoff position 4a of the orthorhombic space group Cmcm and thus exhibit point group symmetry 2̅m... Three of the four M(2N) (N = 1 − 4) atoms forming these icosahedra are pure Ga sites; only M(21) contains very small amounts of In in the ternary rubidium trielides. As expected, the intra-cluster bond lengths r to z (cf. Table 7 for individual values) between all cluster-forming atoms have values of 257 to 279 pm larger than the respective exo-bonds e, d, f, and h. Similar to the structures of the RbGa₇-type, the icosahedra form hexagonal close packed layers (A) in the a-b plane. Along the a axis, they are directly connected via two adjacent exo-bonds h (i.e., via [Ga(24)₄] rings) to form chains running along [100]. In contrast, no direct bonds occur between the icosahedra along [010]; the connection in this direction is achieved by the four-bonded M(2) atoms only. These differences in the icosahedra connectivity lead to a large b:a ratio of approximately 2.52, which deviates strongly from the ideal orthohexagonal ratio of \( \sqrt{3} = 1.73 \). The icosahedra layers are stacked identically (AA) along c, whereby the layers at \( z = 0 \) (A) and \( z = \frac{1}{2} \) (A) are related by, e.g., the mirror plane at \( z = \frac{1}{4} \).

This mirror plane between the icosahedra layers is occupied by layers of [M₁₁] clusters, which are built up by the atoms of the five M(1N) (N = 1−5) sites. Again, this cluster is preferentially formed by gallium. The [M₁₁] clusters of point group m2m symmetry (center at 0, y, \( \frac{1}{2} \)), Wyckoff position 4c) exhibit a closo shape, as all boundary surfaces are (somewhat distorted) triangles. The shape of that half of the cluster formed by the pure Ga-sites is close to an icosahedron, whereas the opposite half around the M(11) position, which is preferentially occupied by the minority substituent In, is strongly distorted. The endohedral M−M bonds (i to q) are again always longer than the exo-bonds (a, b, e-g; Table 7). The largest endohedral bonds j of 282–299 pm (and the large angles \( \angle(Ga–M(11)–Ga) \) of up
to 160°) illustrate the distortion of the closo cluster in the vicinity of the M(11) atoms. The indented shape of the cluster around this position and the therewith increased bond lengths around M(11) are evidently relevant for the Ga/In distribution in the In-substituted derivatives of the K₃Ga₁₃-type structure (cf. the further discussion in Section 3.4). Similar to the icosahedra, the [M₁₁] clusters are also directly exo-bonded along the a axis via four-membered rings (exo-bonds q, Ga(15)–Ga(15)). Along b, additional M atoms (in this case, the three-bonded M(1) atoms) are connecting the clusters. The two [M₁₁] cluster layers per unit cell are related by inversion centers, and their shift relative to the icosahedra layers A is similar to a B and C stacking of a close sphere packing. Thus, the cluster centers are overall stacked along c according to |ABA'C|.

In an alternative description of the structure, the short direct exo-bonds f (along c) and h and q (along a) are connecting the two cluster types to undulated 4× sheets (D) running in the a–c plane around y = 0 and y = 1/2 (cf. the dashed magenta lines in Figure 2). Along b, the stacking sequence |DD'| follows the unit cell C-centering. In this direction, the cluster layers are connected by the additional atoms M(1) and M(2) only.

The tetrahedrally bonded M(2) atoms (8f, two atoms per 2 f.u.) are connecting three icosahedra via the strong bonds c (2×) and d and one [M₁₁] cluster (bond e). The corresponding bond lengths are among the shortest found within the polyanionic network (253–266 pm; Table 8). In the rubidium compounds, for which the pure gallide is not known, this position is nevertheless partly (19–38%) occupied by In, which evidently expands the structure to fit the larger Rb⁺ cations and thus stabilize also a Rb phase of this structure type. With respect to the |ABA'C| cluster packing, the M(2) atoms take one half of the tetrahedral voids.
| Label | Freq. | CN | Distance (pm) | Distance (pm) |
|-------|-------|---|--------------|--------------|
| Ga(12) | 13 | 276.3(1) | 278.8(1) | 274.5(3) | 276.6(3) | 278.29(9) |
| In(12) | 13 | 289.2(1) | 282.8(1) | 295.9(2) | 298.6(2) | 284.18(6) |
| Hg(12) | 13 | 258.2(1) | 257.6(3) | 258.0(3) | 258.44(8) | |
| Ga(21) | 21 | 272.1(1) | 274.0(1) | 276.5(2) | 276.2(2) | 278.64(7) |
| Ga(22) | 21 | 267.9(1) | 269.1(3) | 269.8(3) | 263.93(8) | |
| Hg(21) | 21 | 263.1(1) | 260.1(1) | 265.7(2) | 267.4(2) | 261.23(6) |
| Ga(23) | 12 | 268.4(1) | 269.1(1) | 267.4(2) | 268.1(2) | 268.76(6) |
| Ga(24) | 12 | 270.5(1) | 267.9(1) | 273.9(2) | 273.8(2) | 270.56(6) |
| Ga(25) | 12 | 256.7(1) | 256.6(1) | 258.8(2) | 259.5(2) | 257.00(5) |
| Ga(26) | 12 | 271.8(1) | 273.5(1) | 272.7(2) | 273.5(2) | 273.98(7) |
| Ga(27) | 12 | 280.8(1) | 283.4(1) | 282.0(3) | 282.6(3) | 283.73(8) |
| Ga(28) | 12 | 284.7(2) | 288.4(2) | 289.5(3) | 290.2(2) | 291.84(8) |
| Ga(29) | 12 | 335.2(2) | 338.0(1) | 345.4(2) | 348.3(2) | 346.14(7) |
| Ga(30) | 12 | 345.1(2) | 349.4(3) | 355.8(4) | 357.9(4) | 359.06(4) |
| Ga(31) | 12 | 358.6(2) | 360.1(2) | 365.8(3) | 368.1(3) | 366.62(9) |
| Ga(32) | 12 | 355.7(1) | 355.1(1) | 361.2(1) | 362.3(1) | 359.06(4) |
| Ga(33) | 12 | 367.8(1) | 366.5(1) | 374.3(1) | 375.2(1) | 370.62(4) |
| Ga(34) | 12 | 380.3(2) | 383.2(2) | 386.9(3) | 388.3(3) | 386.77(6) |
| Ga(35) | 12 | 397.3(2) | 400.9(1) | 405.4(3) | 404.8(3) | 407.99(9) |
| Ga(36) | 12 | 399.4(2) | 403.5(1) | 405.1(3) | 410.3(3) | 405.79(9) |
| Ga(37) | 12 | 326.9(2) | 329.2(1) | 334.9(2) | 336.3(2) | 335.50(6) |
| Ga(38) | 12 | 363.4(1) | 371.2(1) | 372.0(1) | 367.45(4) | |
| Hg(22) | 13 | 263.0(1) | 269.7(1) | 263.2(2) | 263.7(2) | 263.67(6) |
| Hg(23) | 13 | 256.1(1) | 257.1(1) | 262.1(3) | 264.7(3) | 261.25(8) |
| Hg(24) | 13 | 281.8(1) | 283.3(1) | 282.0(3) | 282.6(3) | 283.73(8) |
| Hg(25) | 13 | 278.2(1) | 282.8(1) | 278.9(2) | 282.8(2) | 286.5(2) |
| Hg(26) | 13 | 286.6(1) | 289.4(1) | 282.8(2) | 282.8(2) | 286.5(2) |
| Hg(27) | 13 | 271.4(1) | 273.5(1) | 272.7(2) | 273.5(2) | 273.98(7) |
| Hg(28) | 13 | 288.1(1) | 291.4(1) | 287.8(2) | 287.8(2) | 291.4(1) |
| Hg(29) | 13 | 279.0(1) | 282.1(1) | 279.0(2) | 279.0(2) | 282.1(1) |
| Hg(30) | 13 | 286.7(1) | 289.4(1) | 282.8(2) | 282.8(2) | 286.5(2) |
| Hg(31) | 13 | 297.0(1) | 300.7(1) | 297.0(2) | 297.0(2) | 300.7(1) |
| Hg(32) | 13 | 273.8(1) | 276.7(1) | 279.0(2) | 279.0(2) | 282.1(1) |
| Hg(33) | 13 | 287.8(1) | 291.4(1) | 287.8(2) | 287.8(2) | 291.4(1) |
| Hg(34) | 13 | 300.3(1) | 303.9(1) | 300.3(2) | 300.3(2) | 303.9(1) |
| Hg(35) | 13 | 264.7(1) | 267.4(1) | 267.4(2) | 267.4(2) | 267.4(1) |
| Hg(36) | 13 | 273.8(1) | 276.7(1) | 279.0(2) | 279.0(2) | 282.1(1) |
| Hg(37) | 13 | 287.8(1) | 291.4(1) | 287.8(2) | 287.8(2) | 291.4(1) |
| Hg(38) | 13 | 300.3(1) | 303.9(1) | 300.3(2) | 300.3(2) | 303.9(1) |
Table 8. Selected interatomic distances/pm of the K and Rb atoms (top), as well as M(1) and M(2) (bottom) in the crystal structures of compounds forming the K$_3$Ga$_{13}$-type structure (intra-cluster bonds; cf. Table 7).

| Atoms | Distance in Label | Freq. | CN |
|-------|------------------|-------|----|
|       | K$_3$Ga$_{12.48}$In$_{0.15}$ |       |    |
|       | K$_3$Ga$_{12.68}$H$_{0.35}$ |       |    |
|       | Rb$_3$Ga$_{12.35}$In$_{0.68}$ |       |    |
|       | Rb$_3$Ga$_{11.93}$In$_{1.07}$ |       |    |
|       | Rb$_3$Ga$_{12.56}$H$_{0.42}$ |       |    |

| A(1)  |       |       | 2× |
|-------|-------|-------|----|
| - Ga(15) | 343.1(2) | 344.7(1) | 351.1(2) | 353.5(2) | 350.5(1) |
| - Ga(13) | 344.3(2) | 346.6(1) | 352.5(3) | 354.6(3) | 353.5(1) |
| - Ga(22) | 358.6(2) | 360.1(2) | 365.8(3) | 368.1(3) | 366.6(1) |
| - Ga(14) | 367.8(2) | 366.3(1) | 376.5(3) | 379.1(2) | 373.0(1) |
| - M(12)  | 384.5(1) | 385.5(1) | 390.4(2) | 392.4(2) | 387.9(1) |
| - M(1)   | 394.7(1) | 387.8(1) | 401.5(2) | 403.9(2) | 390.8(1) |
| - A(2)   | 362.2(3) | 366.6(2) | 365.9(3) | 368.5(3) | 367.5(1) |
| - A(3)   | 397.0(2) | 395.7(1) | 397.8(2) | 400.8(2) | 395.8(1) |
| - A(11)  | 404.7(2) | 408.4(2) | 409.5(3) | 410.2(2) | 411.9(1) |
| - A(21)  | 404.6(2) | 405.3(1) | 409.8(2) | 411.2(4) | 408.7(1) |

| A(2)  |       |       | 14 + 4 |
|-------|-------|-------|--------|
| - Ga(24) | 326.9(2) | 329.2(1) | 334.9(2) | 336.3(2) | 335.5(1) |
| - Ga(23) | 335.2(2) | 338.0(1) | 345.4(2) | 348.3(2) | 346.1(1) |
| - M(2)   | 353.6(1) | 352.0(1) | 358.4(1) | 360.1(1) | 354.6(1) |
| - A(1)   | 362.2(3) | 366.6(2) | 365.9(3) | 368.5(3) | 367.5(1) |
| - Ga(15) | 366.6(2) | 365.3(1) | 368.5(2) | 371.3(2) | 366.3(1) |
| - M(21)  | 367.8(1) | 366.5(1) | 374.3(1) | 375.2(1) | 370.6(1) |
| - A(11)  | 382.5(1) | 381.4(1) | 383.8(1) | 386.1(2) | 381.6(1) |
| - M(21)  | 397.2(2) | 400.9(1) | 374.3(1) | 375.2(1) | 408.0(1) |
| - A(3)   | 401.7(3) | 405.7(2) | 409.1(3) | 411.0(3) | 412.3(1) |

| A(3)  |       |       | 13 + 2 |
|-------|-------|-------|--------|
| - M(1)  | 330.7(2) | 327.2(1) | 330.6(2) | 331.7(2) | 327.8(1) |
| - Ga(24) | 336.3(2) | 339.3(1) | 345.0(2) | 344.7(2) | 346.8(1) |
| - Ga(22) | 355.7(1) | 355.1(1) | 361.2(1) | 362.3(1) | 359.0(1) |
| - M(2)   | 358.8(2) | 363.9(1) | 363.7(3) | 366.9(3) | 366.4(1) |
| - Ga(23) | 360.2(2) | 362.6(1) | 364.5(2) | 365.2(2) | 365.6(1) |
| - M(13)  | 365.2(1) | 363.4(1) | 371.2(1) | 372.0(1) | 367.4(1) |
| - Ga(15) | 376.4(2) | 372.1(1) | 384.6(2) | 384.7(2) | 384.5(1) |
| - Ga(14) | 377.0(2) | 370.0(1) | 383.0(2) | 385.2(2) | 373.3(1) |
| - A(1)   | 397.0(2) | 396.7(1) | 397.8(2) | 400.8(2) | 395.8(1) |
| - M(12)  | 399.4(2) | 403.5(1) | 405.1(3) | 407.0(1) | 405.8(1) |
| - A(2)   | 401.7(3) | 405.7(2) | 409.1(3) | 411.0(3) | 412.2(1) | 15 + 3
Table 8. Cont.

| Atoms   | Distance in (Å) | Label | Freq. | CN |
|---------|-----------------|-------|-------|----|
|         | $K_3Ga_{12.85}In_{0.15}$ | $K_3Ga_{12.66}Hg_{0.35}$ | $Rb_3Ga_{12.32}In_{0.68}$ | $Rb_3Ga_{11.93}In_{1.07}$ | $Rb_3Ga_{12.58}Hg_{0.42}$ |
| $M(1)$  |                 |       |       |     |
| - M(11) | 250.0(2)        | 249.6(1) | 257.3(4) | 261.0(4) | 253.1(1) | a | 2× |
| - Ga(14)| 254.2(1)        | 260.5(1) | 255.7(3) | 256.3(3) | 264.1(1) | b | 2× |
| - A(3)  | 330.7(2)        | 327.2(1) | 330.6(2) | 331.7(2) | 327.8(1) | 4× | 3 + 6 |
| - A(1)  | 394.7(1)        | 387.8(1) | 401.5(2) | 403.9(2) | 390.8(1) | 4× | 3 + 6 |
| $M(2)$  |                 |       |       |     |
| - Ga(23)| 252.8(1)        | 253.7(1) | 257.4(2) | 259.6(2) | 256.3(1) | c | 2× |
| - M(21) | 256.1(1)        | 257.1(1) | 262.1(3) | 264.7(3) | 261.3(1) | d | 2× |
| - M(12) | 257.5(1)        | 255.3(1) | 264.1(3) | 266.2(3) | 260.2(1) | e | 2× |
| - A(2)  | 353.6(1)        | 352.0(1) | 358.4(1) | 360.1(1) | 354.6(1) | 2× | 2 + 3 |
| - A(3)  | 358.8(2)        | 363.9(1) | 363.7(3) | 366.9(3) | 366.4(1) | 4 + 3 |
The atoms \( M(1) \) at the Wyckoff position 4\( c \) (i.e., one \( M(1) \) per 2 f.u.), which is the only position taken by mercury in the ternary Hg-substituted derivatives, exhibit a pseudo-trigonal planar geometry. The very short bonds \( a \) (250–261 pm) and \( b \) (254–264 pm, Table 8) connect three \([M_{11}]\) clusters. \( M(1) \) is thus located within the B/C \([M_{11}]\) cluster layers taking the common trigonal face of two tetrahedral voids in the h.c.p. stacked slabs of the cluster arrangement.

Three crystallographically different K/Rb cations are incorporated in the polyanionic network, each of them located at an \( 8f \) position. Their CCPs are depicted as yellow polyhedra at the left-hand side of Figure 2. The \( A(1) \) cations are coordinated by 14 triel atoms, of which 12 \( M \) atoms belong to four different clusters. They thus occupy one-half of the tetrahedral voids of the cluster packing. The K/Rb atoms \( A(2) \) and \( A(3) \) with similar coordination numbers of 13 and 15 jointly occupy one large octahedral void within the cluster arrangement, which is accordingly, as described above, elongated along the \( b \) axis. Thus, the occupation of the \( N \) (two per doubled f.u. \( A_6M_{26} \)) octahedra and the 2\( N \) (4) tetrahedra voids between \( N \) (2) clusters can be summarized to:

\[
\begin{array}{c}
\frac{1}{2}\text{tetrah. v.} & \text{octah. voids} & \frac{1}{2}\text{tetrah. v.}
\end{array}
\]

The shortest K–M distances within the CCPs amount to 340 to 345 pm; the respective values for the Rb phases are only slightly larger (350 to 354 pm; Table 8). These somewhat shorter distances compared to those in the RbGa\(_7\)-type compounds, the decreased coordination numbers (13, 14 and 15) compared to 15 + 3 for the RbGa\(_7\)-type, and the volume differences of the CCPs (RbGa\(_7\): 178.6×10\(^6\) pm\(^3\); K\(_5\)Ga\(_{13}\): 163.9 [K(1)], 155.5 [K(2)] and 145.0×10\(^6\) pm\(^3\) [K(3)]) are in accordance with the observation that the latter structure type occurs only with the larger cations Rb\(^+\) and Cs\(^+\). The K\(_5\)Ga\(_{13}\)-type is formed with the smaller cations K\(^+\) and Rb\(^+\), for the latter cation only with a small In/Hg content expanding the polyanion. Similar to the RbGa\(_7\)-type structure, this expansion primarily concerns the distances between the \( \text{exo} \)-bonded cluster layers D (\( b \) direction), as the larger In and Hg atoms mainly take the \( \text{inter} \)-cluster sites (cf. the discussion of the Ga/In/Hg site preferences in Section 3.4).

### 3.3. Electronic Structures of the Pure Gallides

Both structure types of the Ga-rich gallides presented within this work are formally electron-precise compounds, if the Zintl concept is extended by Wade’s electron counting rules.

1. For the RbGa\(_7\)-type, the ionic separation:

\[
2\text{RbGa}_7 \rightarrow 2\text{Rb}^+ + 2^4\text{[Ga(1)]}^- + \text{[Ga}_{12}]^0
\]

reveals that the four-bonded Ga(1)\(^-\) atoms of the dumbbells already equalize the cation charge. The \([\text{Ga}_{12}]\) icosahedra carry no formal charge, as they are connected via triangular closed 2e3c bonds, similar to the bonding situation within the icosahedra layers of elemental \( \alpha \)-rhombohedral boron.

2. For the K\(_5\)Ga\(_{13}\)-type structure:

\[
2\text{K}_5\text{Ga}_{13} \rightarrow 6\text{K}^+ + 3^4\text{[Ga(1)]}^0 + 2^4\text{[Ga(2)]}^- + \text{[Ga}_{12}]^{2-} + \text{[Ga}_{11}]^{2-}
\]

shows that the charge of six cations (per 2 f.u.) is compensated by the two types of \( \text{closo} \) clusters (both \( q = -2 \)) and again two tetrahedrally bonded Ga(2)\(^-\) atoms. Ga(1)\(^0\), with a trigonal-planar coordination, carries no charge and is thus electron-deficient.

Although the chemical bonding in both compounds thus seems to be straightforward and one expects closed-shell compounds with (pseudo) band gaps, both structures show different discrepancies and unexpected features, which are worth a closer inspection:

1. The calculated DOS of CsGa\(_7\) and CsGa\(_7\)In (Figure 3; cf. Section 2.3 and Table 9 for the details of the band structure calculations) unexpectedly exhibit no (pseudo) band gaps, but show a broad minimum of the tDOS clearly below the Fermi level.
2. Conversely, \( \text{K}_3\text{Ga}_{13} \) is indeed the expected semiconductor with a (DFT immanent as well) small band gap (cf. tDOS in Figure 4). Thus, in this case, the possibility of a Ga\( \rightarrow \)Hg exchange is against the expectation.

Figure 3. Total (top) and partial Ga-\( s \) (red) and Ga-\( p \) (blue) density of state (DOS) of CsGa\textsubscript{7}, together with the total DOS (tDOS) and the In(1) partial DOS (pDOS) of “CsGa\textsubscript{6}In” (thin lines).

Figure 4. Total (top) and partial Ga-\( s \) (red) and Ga-\( p \) (blue) DOS of K\textsubscript{3}Ga\textsubscript{13}, together with the tDOS and the Hg(1) pDOS of “Rb\textsubscript{6}Ga\textsubscript{25}Hg” (thin lines).
Both for CsGa$_7$ and K$_3$Ga$_{13}$, the broad valence band region of approximately 12 eV in width is formed by Ga-$s$ and -$p$ states. The pDOS of selected Ga atoms show very similar dispersion, shape, and $s/p$ mixing for the tetrahedrally bonded Ga$^-$ atoms Ga(1)/Ga(2) (in CsGa$_7$/K$_3$Ga$_{13}$). The cluster-forming atoms (e.g., Ga(2) and Ga(3)/Ga(24) as an example in K$_3$Ga$_{13}$) exhibit a larger band dispersion and a stronger mixing of $s$ and $p$ states, with a pronounced pDOS of those $p$ states, which contribute to $exo$-bonds, directly below $E_F$. The pDOS of In(1) in “CsGa$_3$In” (thin lines in Figure 3) does not deviate significantly from Ga(1) in the pure gallide, which shows the very similar bonding features of the heavier triel (see the discussion in Section 3.4).

The calculated valence electron densities ($\rho$) and the results of their Bader analyses fit those of the trielides $A$$M_3$ and $A_2$$M_3$ discussed in [22], as well as those of the complex cluster structure of K$_3$Ga$_{9.6}$In$_{1.4}$ [25]: all $endo$- and $exo$-hedral Ga–Ga bonds carry bond critical points (cf. the individual values in Table 9); ring and cage critical points are again located at the triangular faces and the cluster centers, respectively. For both $exo$- and $endo$-hedral bonds, the bond lengths ($d$) and the electron densities ($\rho_{BCP}$) are correlated, and the absolute values fit the values plotted in Figure 7 of [25]. The associated Laplacians ($\nabla^2 \rho_{BCP}$) are negative for all 2e2c $exo$-bonds. The positive sign for the $endo$-hedral Ga–Ga bonds indicates the delocalized (polyaromatic) character of the cluster shell (cf. the discussion in [25]). The Bader charges ($q$) and volumes ($V_{BB}$) of the atomic basins are also in line with the expectations (cf. Table 9): All alkali cations carry positive charges of $+0.66$ to $+0.74$. All Ga atoms are negatively charged ($−0.05$ to $−0.24$), whereby the small differences are mainly due to the varying number (and distance) of the coordinating $A$ cations and are particularly independent of the formal charges obtained from the above-mentioned ionic partitioning.
Table 9. Details of the calculation of the electronic structure of the binary alkali trielides CsGa$_7$ and K$_5$Ga$_{13}$ ($r_{MT}$: muffin tin radius; $K_{\text{max}}$: maximal wavevector for the PW in the interstitium; BCP: bond critical point; IBZ: irreducible part of the Brillouin zone; $V_{BB}$: volume of the Bader basins; $d$: bond lengths).

| Compound | CsGa$_7$ | ‘CsGa$_6$In’ | a-rhom.B | K$_5$Ga$_{13}$ | ‘Rb$_3$Ga$_{12.5}$Hg$_{0.5}$’ |
|----------|----------|--------------|----------|---------------|-----------------------------|
| Crystal data | | Tables 2 and 3 | [35] | Tables 6 and 5 | |
| $r_{MT}$ (all atoms) | 121.7 pm (2.3 a.u.) | 79.4 pm (1.5 a.u.) | 121.7 pm (2.3 a.u.) | 768 | 144 |
| $r_{MT}$-$K_{\text{max}}$ | 8.0 | | | |
| $k$-points/BZ | 9261 | | | |
| $k$-points/IBZ | 891 | | | |
| Monkhorst-Pack-Grid | $21 \times 21 \times 21$ | | $16 \times 16 \times 3$ | |
| DOS plot | | Figure 3 | | Figure 4 |
| Band structure plot | | Figure 5 | | Figure 5 |

Atoms:

| Charge distribution | label | Charge after Bader | (V$_{BB}$ [10$^6$ pm$^3$]) |
|---------------------|-------|-------------------|-----------------------------|
| CsGa$_7$ | A(1) | +0.662 (35.3) | +0.666 (36.3) |
| | A(2) | - | - |
| | A(3) | - | - |
| Ga/In/Hg(1) | -0.095 (24.7) | -0.060 (29.4) | -0.092 (20.9) |
| Ga(2) | -0.109 (22.4) | -0.132 (22.6) | +0.082 (7.01) |
| Ga(3) | -0.080 (18.7) | -0.071 (19.0) | -0.082 (7.65) |
| Ga(11) | - | - | -0.109 (23.7) |
| Ga(12) | - | - | -0.201 (26.8) |
| Ga(13) | - | - | -0.141 (22.8) |
| Ga(14) | - | - | -0.244 (23.4) |
| Ga(15) | - | - | -0.195 (23.4) |
| Ga(21) | - | - | -0.047 (23.6) |
| Ga(22) | - | - | -0.179 (22.7) |
| Ga(23) | - | - | -0.165 (22.7) |
| Ga(24) | - | - | -0.197 (20.9) |

Bonds:

| Electron density at BCP [e$^{-10^{-6}}$ pm$^{-3}$] | label | a | b | c | d | e | f | g/m |
|-------------------------------------------------|-------|---|---|---|---|---|---|-----|
| (d [pm]) |       | 0.343 (258.3) | 0.334 (258.9) | 0.292 (263.9) | 0.241 (278.7) | 0.236 (282.9) | 0.332 (254.5) | 0.296 (262.4) |
| 0.337 (275.4) | 0.338 (266.5) | 0.290 (264.6) | 0.260 (272.9) | 0.242 (281.2) | 0.327 (255.6) | 0.287 (264.6) | 0.287 (264.6) |
| 0.817 (180.7) | 1.078 (166.8) | 0.817 (180.7) | 0.790 (175.4) | 0.765 (179.9) | 0.791 (178.4) | 0.529 (202.2) | 0.529 (202.2) |
| - | 0.357 (254.2) | 0.373 (252.8) | 0.359 (256.1) | 0.339 (257.5) | 0.382 (250.9) | 0.284 (266.8) | 0.284 (266.8) |
| 0.386 (250.0) | 0.420 (253.1) | 0.355 (264.1) | 0.329 (261.3) | 0.323 (260.2) | 0.364 (253.6) | 0.282 (266.2) | 0.282 (266.2) |
1. Although this partitioning suggests the closed-shell character for both Ga-rich gallides, CsGa\textsubscript{7} and its In-derivative show no (pseudo) band gaps. Instead, the broad minimum of the tDOS between \(-0.55\) and \(-0.05\) eV is due to a steep Ga(3)-\(p_x'\)-type band crossing the Fermi level (cf. the Ga(3)-\(p_x'\) fatband representation of the band structure in Figure 5a; note the orientation of the local coordinate system ‘ at Ga(3) in Figure 5e). The shape of the \(E\)-selected (\(E = -0.23\) to \(-0.36\) eV) valence electron density (dark blue surfaces in Figure 5d) fits the schematic illustration of Ga(3)-\(p_x'\) orbitals exhibiting the \(\sigma\)-bonding character within the six-membered “equator” of the icosahedra layer (Figure 5e). The electron density in the equivalent plot of \(\alpha\)-rhombohedral boron \(E_{\text{min}} = -0.66\) eV) shows a very similar shape. In turn, flat Ga(3)-\(s\) states with small \(\sigma\)-bonding features within the [Ga(3)]\textsubscript{3} rings (cf. the cyan surfaces in Figure 5c) are shifted down the Fermi level at the M and K point of the hexagonal Brillouin zone, which results in the unexpected large DOS at \(E_F\). The population of these states, as well as the depopulation of the Ga(3)-\(p_x'\) band, which exhibits the \(\pi\)-antibonding character within the 2e3c [Ga\textsubscript{3}] triangle, evidently contributes to the differences of the bonding in CsGa\textsubscript{7} and \(\alpha\)-rhombohedral boron: For the latter, the edges of the B\textsubscript{3} ring (g; 202 pm) are much larger than all other \(exo\)- and \(endo\)hedral B–B bonds (cf. the discussion in [44] and the references therein), whereas the triangle of the 2e3c bond (edge g) in CsGa\textsubscript{7} is even somewhat shorter than the \(intra\)-cluster bonds/icosahedra edges (cf. small inset table in Figure 5). The two Fermi surfaces of the bands intersecting \(E_F\) are a homogeneous tube along \(\Gamma-Z\) corresponding to the steep Ga(3)-\(p_x'\) band and a complicated surface at the K/M border of the Brillouin zone, which belongs to the Ga(3)-\(s\) states at the Fermi level. The two surfaces are well separated, and superconducting properties are not to be expected (and not yet examined).

2. The much more complex band structure of K\textsubscript{3}Ga\textsubscript{13} shows the expected “zero” band gap (cf. tDOS in Figure 4). The pronounced tDOS directly above \(E_F\) exhibits the Ga(1)-\(p_z\) character only and thus represents the empty orbital of the trigonal-planar coordinated electron-deficient Ga(1). In the Hg\textsubscript{8}-substituted derivative, where Hg takes exactly this site, these states are accordingly missing (cf. the tDOS of the model system Rb\textsubscript{6}Ga\textsubscript{25}Hg in Figure 4, green line).

Figure 5. Comparison of the band structures of CsGa\textsubscript{7} (a), Ga(3)-\(p_x'\) fatband plot) and \(\alpha\)-rhombohedral boron (b), B(2)-\(p_x'\) fatband plot; (c,d): \(E\)-selected \(\rho\) maps (\(-0.23\) to \(E_F\) and \(-0.23\) to \(-0.36\) eV, cf. the cyan and blue line in the band structure plot (a)) within the 3.4.6.4. net of Ga(3)/B(2) atoms together with (e) a schematic illustration of the Ga(3)-\(p_x'\) orbital bonding contribution at the \(\Gamma\) point (please note the local coordinate ‘ system for Ga(3)).
3.4. Aspects of In/Hg Distribution ("Coloring")

On the Ga→In/Hg exchange, the sizes of the anion atoms $M$ increase by approximately 25/16 pm (metallic radius $r_M$ after Gschneider: 141.1/166.3/157.3 pm for Ga/In/Hg [45]). In the case of In, the electronegativity ($\chi$) decreases marginally (from 1.81 to 1.78 after Pauling [46]), whereas Hg exhibits an increased value of 2.00. These variable atomic properties become apparent in the results of the calculations of the weakly-substituted model variants CsGa$_x$In and Rb$_x$Ga$_{25-2x}$Hg, where the changed $M$ sites exhibit larger Bader basins $V_{BB}$ for both In and Hg, whereas the negative charges $-q_{BB}$ are increased for Hg only (Table 9).

Due to the comparatively small amounts of substituting elements In or Hg, the Bader charges and volumes calculated for the binary gallides CsGa$_7$ and K$_2$Ga$_{13}$ may suggest the “coloring” of the polyanion, i.e., the positions preferentially taken by the larger/more electronegative $M$ atoms. Accordingly, in the case of K$_3$Ga$_{13}$, the Ga position with the largest atomic basin and one of the most pronounced negative charges (due to its sixfold coordination by $A^+$ cations) is selectively occupied by Hg [M(1)]. In contrast, the preferred position for a Ga→In substitution is not straightforward for both title compounds, even though the site occupations are also quite selective. Here, geometric arguments, i.e., (i) a possible expansion of the 3D polyanion and (ii) the avoidance of an incorporation of the larger “doping” elements in the stiff (parts of the) closo clusters are evidently the main parameters for the “coloring” of the 3D triel polyanion:

1. For example, the sizes and charges of the three Ga sites in CsGa$_7$ are very similar (Table 9), but indium strongly prefers the tetrahedral “dumbbell” position $M(1)$ and therewith expands the structure mainly along the most flexible direction, i.e., perpendicular to these layers of tightly connected [Ga$_{12}$] icosahedra. The positions within these layers, especially the central 3.4.6.4. nets containing the six-membered “equators” of the icosahedra, do not accommodate any In atoms.

2. Similar arguments apply to the preferred mixed sites in the K$_3$Ga$_{13}$-type structure: the substitution of Ga by In occurs at the “extra” positions $M(1)$ and $M(2)$, which are connecting the cluster layers $D$ along the $b$ axis, and mainly at the indented position $M(11)$ of the [M$_{11}$] closo cluster, which exhibits comparable large $M$–Ga bonds (i and j; Table 7). The simultaneous occupation of these sites allows for a slight expansion of the structure perpendicular to the layers $D$, i.e., along [010] (cf. the structure description in Section 3.2).

The fact, that—for both structure types—the maximum amount of In increases with the size of the $A$ cations also corroborates the relevance of such geometric parameters for the Ga/In “coloring” in 3D polyanions. The preference of heteropolar bonds, which is the most dominating factor for the “coloring” in polyanions consisting of similar amounts of two atom types with different electronegativities [9,21,47], plays no part in the slightly substituted title compounds.

3.5. Comparison with Other In-/Hg-/Au-Containing Gallides

The coloring pattern observed for CsGa$_7$ also meets the observation for the complex structure of the mixed Ga/In trielides K$_x$Ga$_{11-x}$In$_x$, where indium also occupies all four-bonded inter-cluster sites; in this case, its presence is even crucial for the formation of this type of complex polyanion [25].

The RbGa$_3$-type, which is known for K, Rb, and Cs gallides, also exhibits a 3D network of all-exo-bonded closo clusters, in this case, [Ga($2,3)_8$] dodecahedra, which are connected by direct inter-cluster exo-bonds and further 4b Ga(1) $^-$ [5,6,14,48]. The maximum possible In content $x$ in A(Ga$_{1-x}$In$_x$)$_3$ again decreases with the decreasing size of the counter cation ($x=1/0.3/0.08$ for Cs/Rb/K). Indium prefers to occupy the $M(2)$ position in the “equator” of the dodecahedra, which connects the clusters to layers via long exo-bonds. The four-bonded site $M(1)$ connecting the cluster layers is occupied in second place (e.g., In content in RbGa$_{2.08}$In$_{0.92}$: $M(1/2/3) = 30/56/59$). Band structure calculations of RbGa$_3$ again yielded closely similar Bader volumes for the three different atom types, whereas the four-bonded Ga(1) exhibits a decreased negative charge [22]. As already discussed by Henning and Corbett [23], the “coloring” in RbGa$_3$ is determined by the preservation of the short strong
Ga–Ga bonds \((d_{\text{Ga}(3)-\text{Ga}(3)} = 244.2 \text{ pm})\) in the dumbbells at the top and bottom of the dodecahedra. The related \(\pi\)-bonding contributions are most effective for those positions, where the cluster curvature is high. This position takes up indium atoms only at an overall large In content. Similar to the \(K_7\text{Ga}_{13}\) title phase, a transition element derivative with a reduced number of v.e. is reported for \(Rb\text{Ga}_3\) as well [23], even though the compound is again electron precise, and the calculated band structure shows a small band gap accordingly. Here, smaller \((r = 144 \text{ pm})\) and much more electronegative \((\chi = 2.54)\), but electron poorer gold atoms statistically take all three atom positions. In accordance with the importance of size criteria, the site preference of the smaller Au atoms (Au content: \(M(1) > M(3) \gg M(2)\)) is interchanged with respect to that of the larger In atoms (In content: \(M(2) > M(1) \gg M(3)\)). For \(Rb\text{Ga}_3\), the reduced v.e. number causes a pronounced increase of the strong \(\text{Ga}(3)-\text{Ga}(3)\) bonds of the dumbbells within the dodecahedron. The similar, but small Hg content of the \(K_7\text{Ga}_{13}\)-type causes a shift of the Hg-containing three-bonded site \(M(1)\) associated with an increase of the bond \(b\) from 253 to 260.5 pm and the angle \(\text{Ga}(14)-M(1)-\text{Ga}(14)\) from 95.3 to 91°.

For gallides with only partially connected \textit{closo} clusters, indium strongly prefers to take the position of the “non-connecting” atom in the cluster. These sites show the largest \textit{Bader} volumes and carry the most negative charge, as they are coordinated by the maximum number of cations [22]. The inert pair effect (stronger \(s/p\) separation of In compared to Ga) may be an additional parameter for this observation as is the vast number of alkali-rich thallides with isolated cluster anions ([49] and the references therein). This type of indium preference is observed in the ternary mixed Ga/In trielides of the \(Cs_7\text{In}_{13}\)-type, which exhibit single layers of \textit{closo} \([M_7]\) octahedra connected via four \textit{exo}-bonds [50–52]. Indium occupies the two “tips” of the octahedra, which are not involved in the \textit{exo}-bonds [22]. A similar “coloring” applies in the two structures of the new mixed Ga/In trielides (\(Rb/\text{Cs})_2\text{M}_{15}\), which are stabilized by In contents of 33–46% (Rb) and 26–56% (Cs). Here, the polyanions are double layers of \(\text{exo}-\text{bonded pentagonal bipyramidal closo}\) clusters \([M_7]^{3-}\)-connected via four-bonded \(M^-\). Again, In atoms terminate the layers, as they prefer to occupy the “unconnected” corners of the clusters (cf. \(Cs_7\text{In}_{13}\)-type), and the “dumbbells” within the \([M_7]\) polyhedra are formed by Ga atoms exclusively (cf. \(\text{RbGa}_3\)-type).

For mixed Ga/In trielides containing isolated clusters, like the \(Cs_9\text{Ga}_{11}\)-type [10,12], atom sizes are also the most relevant criteria for the Ga→In substitution, and the site with the largest \textit{Bader} volume (and the longest \(M\)-Ga bonds) is preferentially occupied by the larger In atoms. On the other hand, mercury atoms with their increased electronegativity again prefer to take the position with the most negative \textit{Bader} or Mulliken charges [53].

4. Summary

In the course of systematic “coloring” studies of mixed trielides, small amounts of Ga in the binary most Ga richest electron-precise cluster compounds \(Rb\text{Ga}_3/\text{CsGa}_7\) and \(K_5\text{Ga}_{13}/“\text{RbGa}_{13}\)” were substituted by the larger element In and the similarly larger, but also more electronegative and electron poorer Hg. Due to the incongruent melting of all phases, well-developed single crystals were grown from \(Ga/In/\text{Hg}\)-rich melts, and their structures were refined by means of single crystal X-ray data. In \(Rb\text{Ga}_7/\text{CsGa}_7\), up to 9.9/13.6% of Ga could be substituted by In, which occupies up to 80% of the four-bonded \(M_2^{2-}\) dumbbells connecting the a-B like \([Ga_{12}]\) icosahedra layers. In contrast, a Ga→Hg substitution is not possible, which opened up the possibility to crystallize the yet not fully characterized binary hepta-gallides from elemental Hg. Though electron precise, the calculated DOS of \(Cs\text{Ga}_7\) and \(Cs\text{Ga}_7\) unexpectedly exhibit no (pseudo) band gaps. An analysis of the band structures, energy-selected electron densities, and the Fermi surfaces (with a-rhombohedral boron for comparison) shows that Ga(3)-\(p_x\)-like bands with \(\sigma\)-bonding characteristic within the layer of the six-membered “equator” of the icosahedra and the \([Ga_3]\) rings are crossing \(E_F\) and are thus only partly occupied. Conversely, Ga(3)-\(s\) states with \(\sigma\)-bonding features within the \([Ga(3)]_3\) rings are shifted towards the Fermi level and result in the unexpected large DOS at \(E_F\). In \(K_7\text{Ga}_{13}/“\text{RbGa}_{13}\)” , the overall \(1.2/5.2–8.2\%\) of indium mainly fits in the indented position of the \textit{closo} \([Ga_{11}]^{2-}\) clusters, which allow
for larger endohedral M–M bonds. In the Hg-substituted derivatives, the unique, only trigonal-planar bonded Ga(1) \(^{10}\) site is nearly completely substituted by the chemically much different mercury, resulting in an overall Hg content/M of \(2.7/3.2\%\) (for \(A = K, Rb\)). The Ga/In/Hg/(Au) distribution in both types of title compounds is comparable with those in the structures of other 3D anionic networks, in the mixed Ga/In trielides containing cluster layers and in the isolated clusters of the \(Cs_8Ga_{11}\)-type.

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