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The family of LiCo_6P_4 type compounds – Trends in electronic structure and chemical bonding

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Running title: LiCo_6P_4 -type compounds

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Abstract. Selected ternary compounds of the family of AT_6X_4 (LiCo_6P_4 -type) intermetallics have been studied by *ab initio* methods with respect to their electronic structures and chemical bonding. The bonding characteristics highlight the role of the three-dimensional $[\text{T}_6\text{X}_4]$ polyanionic networks which, within the hexagonal channels, accommodate loosely bonded A cations. In alkali metal based compounds, when T is replaced by indium (e. g. in KIn_6Au_4) the reverse occupancy leads to positively charged In ($\sim +0.5$) and negatively charged Au (~ -0.9). Peculiar magnetic behavior is traced out whereby a magnetic order is identified only when T is a 3d element which polarizes and induces a negative small moment on A (U) as in UCr_6P_4 oppositely to CeRh_6X_4 for X = Si, Ge.

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1 Introduction

The complex metal-rich phosphide LiCo_6P_4 [1] is the prototype for a small series of compounds. LiCo_6P_4 crystallizes with space group $P\bar{6}m2$, Pearson symbol hP11 with one formula unit per cell. The structure comprises seven crystallographically independent sites. The representatives [2-7] with the different coloring on these sites are listed in Table 1. The phosphides and arsenides exist for cobalt and rhodium and the cation position of lithium can be substituted also by an alkaline earth metal. A peculiar example is the low-temperature phase of UCr_6P_4 with a distinctly lower valence electron count. Recently the first tetrelides with LiCo_6P_4 type structure were reported; the silicide CeRh_6Si_4 [5] and the series of germanides RERh_6Ge_4 ($\text{RE} = \text{Y}, \text{La-Nd}, \text{Sm-Lu}$) [6, 8]. Thus, compounds with the LiCo_6P_4 type allow for certain flexibility in the valence electron concentration.

This peculiar structure type is built up from a rigid three-dimensional polyanionic network which leaves channels for the cations. The CeRh_6Ge_4 structure is exemplarily presented in Figure 1. The bonding variations in this structure type mainly result from the coloring within the polyanion. A very interesting bonding situation concerns the alkali metal compounds KIn_6Au_4 and RbIn_6Au_4 [7], where the transition metal and p -element atoms exchange their sites, a consequence of the high electronegativity of the gold atoms. Formally one can call KIn_6Au_4 and RbIn_6Au_4 anti-types of LiCo_6P_4 , similar to the well-known relationship perovskite–anti-perovskite.

So far only few of the LiCo_6P_4 type compounds have been studied with respect to their chemical and physical properties. KIn_6Au_4 is a Pauli paramagnet [9] and the germanides RERh_6Ge_4 ($\text{RE} = \text{Ce}, \text{Gd-Yb}$) [6, 8] show Curie-Weiss behavior with experimental magnetic moments close to the free-ion values of RE^{3+} . The highest magnetic ordering temperature of $T_N = 13.6 \text{ K}$ occurs for TbRh_6Ge_4 .

First studies on electronic structure and chemical bonding have been performed for KIn_6Au_4 [7], and LiCo_6P_4 [9]. Both structures show optimized covalent bonding in their $[\text{In}_6\text{Au}_4]^{8-}$ and $[\text{Co}_6\text{P}_4]^{8-}$ polyanionic networks and weaker cation-anion bonding. Total energy calculations of LiCo_6P_4 and the structurally closely related phosphide $\text{Li}_2\text{Co}_{12}\text{P}_7$ indicated stability of the $[\text{Co}_6\text{P}_4]$ and $[\text{Co}_{12}\text{P}_7]$ substructures upon de-lithiation. These

studies were performed in the context of ternary tetrelides and pnictides with potential lithium mobility [10-13].

In extension of our synthetic work on LiCo_6P_4 type compounds we have now studied the electronic structures and chemical bonding of the whole family in the context of DFT based calculations [14, 15], focusing on the electronic structure (density of states, magnetic ground states) as well as trends in the cohesive energies, the atomic charges and the overlap populations providing hints on the properties of chemical bonding.

2 Computational methodologies

Two computational methods within the DFT [14, 15] were used in a complementary manner. The Vienna ab initio simulation package (VASP) code [16, 17] allows geometry optimization and cohesive energy calculations. For this we use the projector augmented wave (PAW) method [17], with the generalized gradient approximation (GGA) scheme following Perdew, Burke and Ernzerhof (PBE) [18]. Semi-core electrons of Li, K, Rb, Mg, Ca, Sr states were considered upon building the respective PAW potentials. Preliminary calculations with local density approximation LDA [19] led to largely underestimated volumes versus the experiment. The conjugate-gradient algorithm [20] is used in this computational scheme to relax the atoms. The tetrahedron method with Blöchl corrections [21] as well as a Methfessel-Paxton [22] scheme was applied for both geometry relaxation and total energy calculations. Brillouin-zone (BZ) integrals were approximated using the special k-point sampling. The optimization of the structural parameters was performed until the forces on the atoms were less than $0.02 \text{ eV}/\text{\AA}$ and all stress components less than $0.003 \text{ eV}/\text{\AA}^3$. The calculations are converged at an energy cut-off of 500 eV for the plane-wave basis set with respect to the k-point integration up to $8 \times 8 \times 13$ (k_x , k_y , k_z) for best convergence and relaxation to zero strains. The calculations are scalar relativistic and assume spin degenerate total spins.

Then all-electron calculations with the GGA were carried out for a full description of the electronic structure and the properties of chemical bonding, using the augmented spherical wave (ASW) method devised by Williams, Kübler and Gelatt in 1979 [23] as a linearized method close to the LMTO (Linearized Muffin Tin Orbitals) method. It has benefited from continuous developments leading to full potential FP-ASW with

implementation of chemical bonding according to different schemes (cf. the text book by V. Eyert [24] and therein references). The ASW method uses a minimal basis set for the valence states with the outermost shells representing one of each kind: the valence states and the matrix elements are constructed using partial waves up to $l_{\max}+1 = 4$ for Ce and U, $l_{\max}+1 = 3$ for T, and $l_{\max}+1 = 2$ for X. Self-consistency is achieved when charge transfers and energy changes between two successive cycles were below 10^{-8} and 10^{-6} eV, respectively. BZ integrations were performed using the linear tetrahedron method within the irreducible wedge. Besides the site projected density of states, we discuss qualitatively the pair interactions based on the overlap population analysis with the crystal orbital overlap population (COOP) [25]. In the plots, positive, negative, and zero COOP indicate bonding, anti-bonding, and non-bonding interactions, respectively.

3 Crystal chemical considerations

Before starting the theoretical description we draw back to the crystal chemical details of the LiCo_6P_4 type phases. This peculiar structure type is realized for several pnictides, but recently also the first tellurides have been reported. The different coloring of the atoms on the seven crystallographically independent sites is summarized in Table 1.

Exemplarily we discuss the CeRh_6Ge_4 structure [6]. The rhodium and germanium atoms build up a rigid three-dimensional polyanionic $[\text{Rh}_6\text{Ge}_4]^{\delta-}$ network which is charge-balanced by the cerium atoms. The latter fill larger cavities within hexagonal channels left by the $[\text{Rh}_6\text{Ge}_4]^{\delta-}$ network (Figure 1). The polyanion exhibits Rh–Ge (247–255 pm) and Rh–Rh (285–291 pm) bonding. The Rh–Ge distances are close to the sum of the covalent radii of 247 pm [26] and the Rh–Rh distances are all slightly longer than in *fcc* rhodium (269 pm) [27]. Similar crystal chemistry can be discussed also for the pnictides. Regarding the Rh–Rh connections it might be relevant to discuss their nature in actual compound. This is illustrated by the plot of the COOP for the rhodium bonding within one substructure and between two substructures Rh1 and Rh2. Fig. 3 shows the plots obtained from self consistent total spins in CeRh_6Ge_4 . The prevailing bonding is found between the Rh1 and Rh2 substructure whereas much weaker and similar COOP are exhibited for Rh1–Rh1 and Rh2–Rh2. Nevertheless the bonding (positive magnitudes along *y* axis) COOP are compensated by antibonding (negative) within the VB so that

the Rh-Rh bonding does not contribute to the stability of the compound. Those are rather the hetero-connections, such as Co-P in MgCo_6P_4 (cf. Fig. 4) which are responsible of the cohesion of the ternary compounds.

An alternative description of the CeRh_6Ge_4 structure is possible via the coordination polyhedra (Fig. 2). The cerium atoms have coordination number (CN) 18 by six germanium and twelve rhodium atoms. These CN18 polyhedra fill the corners of the unit cell and they are stacked along the c axis via common hexagonal faces. The second relevant polyhedron concerns the Ge1 atoms which have CN9 by rhodium atoms. These Ge1@Rh_9 polyhedra fill the space between the corner-sharing (via rhodium atoms) $\text{Ce@Ge}_6\text{Rh}_{12}$ polyhedra.

Besides the classical site occupancy variants, also the alkali metal compounds KIn_6Au_4 and RbIn_6Au_4 [7] with an inverse site occupancy have been reported. Comparing the $[\text{In}_6\text{Au}_4]^{\delta-}$ and $[\text{Co}_6\text{P}_4]^{\delta-}$ networks this switch in site occupancy is readily understandable on the basis of electronegativity arguments, *i. e.* the highly electronegative gold atoms substitute phosphorus, similar to the pairs of compounds $\text{Hf}_2\text{Co}_4\text{P}_3$ *vs.* $\text{Sr}_2\text{In}_4\text{Au}_3$ [28] and YCo_5P_3 *vs.* $\text{Ca}_2\text{In}_4\text{Au}_3$ [29].

The second exception concerns the phosphides ScRh_6P_4 , YbRh_6P_4 , and LuRh_6P_4 [30]. They crystallize with a superstructure of the LiCo_6P_4 type, resulting from two *translationengleiche* symmetry reductions. Small atomic displacements allow for a weak puckering.

Finally we draw our attention to the valence electron count (VEC). Similar to many other families of intermetallics, also the LiCo_6P_4 type phases show a certain stability range. The smallest VEC of 73 occurs for the tetrelides like CeRh_6Ge_4 and the highest one of 79 for the aurides KIn_6Au_4 and RbIn_6Au_4 . Keeping this range and the small number of representatives in mind, several other representatives are likely to exist. Nevertheless, their composition will only be discovered by serendipity.

4 Results and discussion

4.1. Non-magnetic representatives

MgCo_6P_4

Recent DFT investigations of LiCo_6P_4 together with $\text{Li}_2\text{Co}_{12}\text{P}_7$ [9] have shown the particularity in both phosphides to exhibit strong Co–P bonding within the polyanionic networks $[\text{Co}_6\text{P}_4]^{8-}$ and $[\text{Co}_{12}\text{P}_7]^{8-}$, respectively. Less bonding between Li and the polyanions could let suggest a possible Li de-intercalation with favorable energetics.

From Table 2 the geometry optimized crystal structure results are found in relatively good agreement with the experiment for the internal coordinates (Co1, Co2, and P1) although slightly smaller hexagonal lattice parameters a and c are obtained. These trends are also observed for the other compounds studied in this paper.

Then the results can be used to examine energy trends and charge transfers. The cohesive energies can be obtained from the difference between the total electronic energy obtained at self consistent convergence on one hand and those of the atomic constituents Mg, Co and P on the other hand in their ground state structures, i. e. hexagonal for Mg and Co and simple cubic for white phosphorous:

$E(\text{MgCo}_6\text{P}_4) = -72.745$ eV; $E(\text{Mg}) = -1.392$ eV/atom; $E(\text{Co-hexagonal}) = -6.88$ eV/atom and $E(\text{P}) = -5.24$ eV/atom. Taking the respective multiplicities into account, the resulting cohesive energy averaged per atom is $E_{\text{coh.}}(\text{MgCo}_6\text{P}_4) = -0.828$ eV which is found slightly smaller in magnitude than the one obtained for the lithium compound, i. e. $E_{\text{coh.}}(\text{LiCo}_6\text{P}_4) = -0.833$ eV [9]. This is concomitant with the larger electronegativity of Mg ($\chi_{\text{Mg}} = 1.31$ versus $\chi_{\text{Li}} = 0.98$) whereby LiCo_6P_4 is more ionic than MgCo_6P_4 . A more quantitative approach of these features is obtained through the analysis of the electron transfers obtained from charge density analysis using the AIM (atoms in molecules theory) approach [31]. Typically in chemical compound, the charge density reaches a minimum between atoms and this is a natural region to separate them from each other. Such an analysis does not constitute a tool for evaluating absolute ionizations but allows establishing trends between similar compounds. For the Mg and Li based phosphides the average charge values (Q) are:

LiCo_6P_4 :	$Q(\text{Li}) = +0.86$	$Q(\text{Co}) = +0.30$	$Q(\text{P}) = -0.66$
MgCo_6P_4 :	$Q(\text{Mg}) = +1.66$	$Q(\text{Co}) = +0.19$	$Q(\text{P}) = -0.70$

The almost twice larger positive charge carried by Mg arises from its divalent character, i.e. versus monovalent Li. The consequence is a larger positive ionization of

Co in the latter compound so that the negative charge carried by P is almost the same, i.e. close to ~ -0.7 .

In so far as the calculated structure parameters are found close to the experimental values [2], the electronic structure and the properties of chemical bonding are calculated using the latter. They were started assuming spin degenerate non spin polarized (NSP) magnetic configuration. Spin polarized (SP) calculations were carried out for the Ce and U based magnetic compounds which present an instability in such NSP configuration. This is detailed in following sections.

With the all electrons ASW method, at self consistent convergence of the energies and charges, small charge transfers similar to the above trends were obtained. Fig. 4 shows the NSP site projected DOS–PDOS (top) and the chemical bonding (COOP) – bottom– for MgCo_6P_4 . Energy reference along the x axis is with respect to the Fermi level E_F . Due to the large filling of Co already at the atomic state ($4s^2, 3d^7$) the largest part of Co-PDOS are found within the valence band (VB) and crossed by E_F at the upper part. A metallic character can be traced out. The two Co sites (Co1, Co2) have similar PDOS as well as P which follow the shape of the Co PDOS especially in the $\{-7, -3 \text{ eV}\}$ energy window i.e. in the region of the lower energy Co d and P p states which mix leading to the chemical bonding ensuring for the stability of the ternary compound through the $[\text{Co}_6\text{P}_4]^{\delta-}$ entities, whereas the Mg PDOS are vanishingly small due to their itinerant s character. The chemical bonding is discussed based on the overlap population analysis using the COOP scheme [25]. From the lower panel in Fig. 3 the major interactions within the VB are between Co and P through the $[\text{Co}_6\text{P}_4]^{\delta-}$ polyanions; they are of bonding nature (positive COOP). The other contributions, Mg–Co and Mg–P are vanishingly small. This confirms the picture of a system presenting Co/P substructures as building a skeleton in which Li and Mg are loosely bonded within the $[\text{Co}_6\text{P}_4]$ motifs. This feature which is inherent to the LiCo_6P_4 type should be found in all other members considered here with some differences pertaining to reverse site occupancies as in AAu_4In_6 ($A = \text{K, Rb}$) or magnetic polarization with $A = \text{Ce, U}$.

Reverse site occupancies in KIn_6Au_4 and RbIn_6Au_4

The alkali metal compounds KIn_6Au_4 and RbIn_6Au_4 [7] show an inverse site occupancy with respect to the classical site occupancy variants as the Li and Mg

compounds. The electronic structure and bonding properties were studied with the LMTO code by Li and Corbett in 2007 [7] without pointing out to the charge changes that we address here based on Bader analysis of the charge density resulting from PAW-GGA calculations. The energy results and the Bader charge analysis results obtained after the calculations are shown in Table 3.

Clearly the effect of inverse site occupation is reflected in the charges whereby In sites carry positive charges whereas Au is negatively charged. Comparing the $[\text{In}_6\text{Au}_4]^{8-}$ and $[\text{Co}_6\text{P}_4]^{8-}$ networks this switch in site occupancy is readily understandable on the basis of electronegativity arguments, *i. e.* the highly electronegative gold atoms substitute phosphorus. Consequently in these compounds the transition metal position adopts a positive charge whereas Au at X *p* element position is negatively charged. This is helped by the electronegativity magnitudes, larger for Au (2.54) versus In (1.78). The potassium compound is found more cohesive than the Rb one. This can be related to the volume differences $V(\text{KIn}_6\text{Au}_4) = 249.7 \text{ \AA}^3$ versus $V(\text{RbIn}_6\text{Au}_4) = 253.5 \text{ \AA}^3$. Although both K and Rb possess the same Pauling electronegativity of $\chi = 0.82$, there is a larger charge transfer from potassium to the $[\text{In}_6\text{Au}_4]$ polyanionic substructure.

Fig. 5 shows the PDOS (top) and the COOP –bottom– for KIn_6Au_4 . Due to the large filling of Au 5*d* up to ~ 10 electrons, these *d* states are found within the VB. This is also observed for the indium filled *d* states found at -15 eV below E_F . The result is an itinerant electron system with E_F crossing *s,p* like states. Bonding is then expected to be mainly in the energy region around Au *d* states. This is illustrated in the lower panel showing over a narrower energy window for the sake of clarity the COOP for one atom of each kind to enable comparisons. The major bonding is for Au-In (as for Co-P in Fig. 4) at -6 eV as well as below E_F all with mainly bonding character; antibonding COOP being mainly above E_F , whereas the other interactions, K-In and K-Au are of vanishingly small magnitudes. These features resemble those found in the MgCo_6P_4 so that bonding is similar in both in spite of the inverse occupations.

The superstructure of ScRh_6P_4

ScRh_6P_4 [30] is a distorted variant of LiCo_6P_4 . Two possible origins might be put forward to explain this feature:

- a geometrical consequence (puckering) due to the small scandium atoms

– or an electronic structure reason.

The full geometry relaxation calculations show that the ground state is indeed the $P3$ superstructure versus the LiCo_6P_4 type subcell with $\Delta E = -0.045$ eV/cell, i.e. -0.004 eV/at. With this small energy magnitude and the close trends of Bader charges in both forms: $\sim\text{Sc}^{+1.57}$, $\sim\text{Rh1}^{+0.04}$ $\sim\text{Rh2}^{-0.20}$ and $\sim\text{P}^{-0.27}$, the stabilization is more assignable to the puckering induced by the structural change due to size effects. Such geometrical factors have been observed for the superstructure formation of many intermetallic scandium compounds [32].

The large flexibility within the polyanionic networks of the LiCo_6P_4 type compounds readily reminds the large family of half-antiperovskites like $\text{InSn}[\text{Co}_3\text{S}_2]$ or $\text{A}_2[\text{Rh}_3\text{S}_2]$ ($\text{A} = \text{In}, \text{Sn}, \text{Pb}, \text{Tl}$) [33-35] which show similar electronic flexibility, although the sulphide substructure differs from the pnictides and tetrelides reported herein.

4.2. Magnetic representatives based on Ce and U

In the context of the peculiar crystal chemical characteristics of the A atom weakly bonded within the $[\text{T}_6\text{X}_4]$ building blocks, it becomes relevant to examine the effects on the magnetism at the levels of the T as well as the A atoms with $\text{A} = \text{Ce}, \text{U}$.

CeRh₆Si₄ and CeRh₆Ge₄

As shown in Table 4 the calculated charge carried by Ce in both compounds does not give a hint on the valence state of Ce i.e. trivalent or intermediate valent [36]. Within the $[\text{Rh}_6\text{X}_4]$ networks Rh is negatively charged whereas the X atoms (Si and Ge) are positively charged. This follows from the larger Pauling electronegativity χ of Rh (2.28) versus Si (1.9) and Ge (2.01). Using the experimental structure data NSP calculations were carried out with the all electron scalar relativistic ASW method. The site projected DOS (PDOS) plots are shown in Fig. 5. The two panels show similar features pertaining to the presence of Rh 4d states centered around -3 eV below the Fermi level within the VB, and Si, Ge p like states in the energy range $-6.5/-4$ eV mixing with the Rh states. Si, Ge s like states are found at the lowest energy part of the VB. Differences appear at E_F where Ce 4f states are found crossed by E_F at a finite DOS magnitude of $\sim 6 \text{ eV}^{-1}$ in the Ge compound, while they are found well within the CB in

CeRh₆Si₄. This signals a possible magnetic instability for CeRh₆Ge₄ in such a NSP configuration.

SP calculations were subsequently carried out for both compounds. As expected no magnetic solution was found for CeRh₆Si₄ whereas finite magnetization developed ferromagnetically in CeRh₆Ge₄ with small moments magnitudes (moments in Bohr magnetons: μ_B): $M(\text{Ce}) = 0.05$; $M(\text{Rh1}) = 0.16$; $M(\text{Rh2}) = 0.19$; $M(\text{Ge}) \sim 0.006-0.008$; $M(\text{Cell}) = 1.13 \mu_B$. However, larger integration of the BZ led to vanishing values meaning that there is no stable magnetic solution. Although an interpretation of this peculiarity will be provided upon discussing the results for the uranium compound, we develop further on this using complementary GGA+U calculations following the scheme of Dudarev et al. [37] were carried out to test the effect of increasing the correlations of the DFT exchange-correlation functional, GGA. U stands for the Coulomb on-site repulsive parameter added to enhance correlation. The plain GGA scalar relativistic converged calculations are then used with $U = 4$ eV acting on $4f$ states. In both CeRh₆Si₄ and CeRh₆Ge₄, at self consistent convergence and high integration of the BZ, there is no onset of magnetic moment on any constituent, especially Ce. Note that the paramagnetic measured moment of Ce³⁺ is not in contradiction with our findings which only translate the solution of the absence of long range magnetic order. In other words a paramagnetic configuration is not possibly reproduced with SP calculations if no large supercells with random spin orientations are accounted for.

Lastly we mention that the synthesis of larger CeRh₆Ge₄ quantities for neutron diffractions studies is in progress.

UCr₆P₄

NSP calculation results are given for the PDOS at Fig. 6 (top). The uranium $5f$ states are centered well above the Fermi level which crosses Cr $3d$ states at a finite PDOS magnitude close to $\sim 7 \text{ eV}^{-1}$. Then any magnetic instability should arise from the spin polarization of the transition metal (Cr) and not from uranium. Subsequent spin-polarized calculations for UCr₆P₄ led to finite moments (in μ_B):

$$M(\text{U}) = -0.52; M(\text{Cr2}) = 0.94; M(\text{Cr1}) = 1.07; M(\text{P}) \sim 0.006-0.008; M(\text{Cell}) = 5.54$$

and a resulting ferrimagnetic like ground state. As a matter of fact the moment on uranium is carried by the itinerant d and f states which mix with those of Cr d . The (genuine) polarization of the latter induces the moment carried by uranium. This is further reflected by the SP PDOS shown in the lower panel of Fig. 5 for majority ($\uparrow$) and minority ($\downarrow$) spin populations. There is a downwards energy shift of majority Cr $3d$ states, opposed to upward minority whence the moment $m(\text{Cr}) = n(\uparrow) - n(\downarrow)$ whence the appellation of majority versus minority populations. The opposite is observed for uranium whence its negative moment. The difference between the Ce and U compounds is in the nature of the transition metal which shows a trend to developing a magnetic moment when it is of the first period (Cr $3d$) and less tendency to polarize when it belongs the 2nd period as for Rh.

Also further GGA+ U calculations led to the same ferrimagnetic solution with an enhancement of the magnetic moments (in μ_B): $M(\text{U}) = -1.87$; $M(\text{Cr2}) = 0.62$; $M(\text{Cr1}) = 1.15$; $M(\text{P}) \sim 0.06\text{-}0.08$; $M(\text{Cell}) = 3.58$. Neutron diffraction experiments would be needed to clearly establish the magnetic structure.

Summing up, the family of LiCo_6P_4 type compounds exhibits interesting coloring on all positions. Leading to several tetrelides and pnictides and also some antitype compounds like KIn_6Au_4 and RbIn_6Au_4 where the transition metal and p element sites interchange as a consequence of the electronegative range. Chemical bonding analyses nicely underlines the variations within the different polyanionic networks. The LiCo_6P_4 family covers a variety of non-magnetic members but also paramagnetic ones like CeRh_6Si_4 and CeRh_6Ge_4 and the calculations also point to chromium magnetism in UCr_6P_4 .

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References

- [1] R. Buschmann, H.-U. Schuster, *Z. Naturforsch.* **1991**, 46b, 699.
- [2] A. Hellmann, A. Mewis, *Z. Anorg. Allg. Chem.* **2001**, 627, 1357.
- [3] A. Wurth, A. Mewis, *Z. Anorg. Allg. Chem.* **1999**, 625, 449.
- [4] W. Jeitschko, R. Brink, *Z. Naturforsch.* **1992**, 47b, 192.
- [5] A. Lipatov, A. Gribanov, A. Grytsiv, S. Safronov, P. Rogl, J. Rousnyak, Y. Seropegin, G. Giester, *J. Solid State Chem.* **2010**, 183, 829.
- [6] D. Voßwinkel, O. Niehaus, U. Ch. Rodewald, R. Pöttgen, *Z. Naturforsch.* **2012**, 67b, 1241.
- [7] B. Li, J. D. Corbett, *Inorg. Chem.* **2007**, 46, 6022.
- [8] D. Voßwinkel, O. Niehaus, R. Pöttgen, *Z. Anorg. Allg. Chem.* **2013**, 639, 2623.
- [9] S. F. Matar, A. Al-Alam, N. Ouaini, R. Pöttgen, *J. Solid State Chem.* **2013**, 202, 227.
- [10] R. Pöttgen, T. Dinges, H. Eckert, P. Sreeraj, H.-D. Wiemhöfer, *Z. Phys. Chem.* **2010**, 224, 1475.
- [11] A. Kuhn, P. Sreeraj, R. Pöttgen, H.-D. Wiemhöfer, M. Wilkening, P. Heitjans, *J. Am. Chem. Soc.* **2011**, 133, 11018.
- [12] T. Langer, S. Dupke, H. Eckert, S. F. Matar, M. Winter, R. Pöttgen, *Solid State Sci.* **2012**, 14, 367.
- [13] S. F. Matar, R. Pöttgen, *Solid State Sci.* **2012**, 14, 1471.
- [14] P. Hohenberg, W. Kohn, *Phys. Rev.* **1964**, 136, B864.
- [15] W. Kohn, L. J. Sham, *Phys. Rev.* **1965**, 140, A1133.
- [16] G. Kresse, J. Furthmüller, *Phys. Rev. B* **1996**, 54, 11169.
- [17] G. Kresse, J. Joubert, *Phys. Rev. B* **1999**, 59, 1758.
- [18] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, 77, 3865.
- [19] D. M. Ceperley, B. J. Alder, *Phys. Rev. Lett.* **1980**, 45, 566.
- [20] W. H. Press, B. P. Flannery, S. A. Teukolsky, W. T. Vetterling, *Numerical Recipes*, Cambridge University Press, New York, **1986**.
- [21] P. E. Blöchl, *Phys. Rev. B* **1994**, 50, 17953.
- [22] M. Methfessel, A.T. Paxton, *Phys. Rev. B* **1989**, 40, 3616.
- [23] A. R. Williams, J. Kübler, C. D. Gelatt Jr., *Phys. Rev. B* **1979**, 19, 6094.
- [24] V. Eyert, *The Augmented Spherical Wave Method – A Comprehensive Treatment*, Lecture Notes in Physics, Springer, Heidelberg, **2007**.
- [25] R. Hoffmann, *Angew. Chem. Int. Ed. Engl.* **1987**, 26, 846.
- [26] J. Emsley, *The Elements*, Oxford University Press, Oxford, **1999**.
- [27] J. Donohue, *The Structures of the Elements*, Wiley, New York, **1974**.

- [28] R.-D. Hoffmann, R. Pöttgen, C. Rosenhahn, B. D. Mosel, B. Künnen, G. Kotzyba, *J. Solid State Chem.* **1999**, *145*, 283.
- [29] R.-D. Hoffmann, R. Pöttgen, *Z. Anorg. Allg. Chem.* **1999**, *625*, 994.
- [30] U. Pfannenschmidt, U. C. Rodewald, R. Pöttgen, *Monatsh. Chem.* **2011**, *142*, 219.
- [31] R. F. W. Bader, *Chem. Rev.* **1991**, *91*, 893.
- [32] H. Eckert, R. Pöttgen, *Z. Anorg. Allg. Chem.* **2010**, *636*, 2232.
- [33] R. Weihrich, S. F. Matar, V. Eyert, F. Rau, M. Zabel, M. Andratschke, I. Anusca, Th. Bernert, *Prog. Solid State Chem.* **2007**, *35*, 309.
- [34] A. Anusca, Ph. P. Schmid, J. Rothballer, F. Pielnhöfer, R. Weihrich, *Z. Anorg. Allg. Chem.* **2009**, *635*, 2410.
- [35] F. Rothballer, F. Bachhuber, F. Pielnhöfer, F. M. Schappacher, R. Pöttgen, R. Weihrich, *Eur. J. Inorg. Chem.* **2013**, 248.
- [36] S. F. Matar, *Prog. Solid State Chem.* **2013**, *41*, 55.
- [37] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, A. P. Sutton, *Phys. Rev. B* **57** (1998) 1505.

Table 1. Site occupancies for intermetallic compounds with hexagonal LiCo_6P_4 type structure.

Compound	1a	1c	3j	3k	3k	Reference
LiCo_6P_4	Li	P1	Co1	Co2	P2	[1]
MgCo_6P_4	Mg	P1	Co1	Co2	P2	[2]
MgRh_6P_4	Mg	P1	Rh2	Rh1	P2	[3]
UCr_6P_4	U	P1	Cr2	Cr1	P2	[4]
MgRh_6As_4	Mg	As1	Rh2	Rh1	As2	[3]
CaRh_6As_4	Ca	As1	Rh2	Rh1	As2	[3]
SrRh_6As_4	Sr	As1	Rh2	Rh1	As2	[3]
YbRh_6As_4	Yb	As1	Rh2	Rh1	As2	[3]
CeRh_6Si_4	Ce	Si1	Rh2	Rh1	Si2	[5]
CeRh_6Ge_4	Ce	Ge1	Rh2	Rh1	Ge2	[6]
KIn_6Au_4	K	Au1	In2	In1	Au2	[7]
RbIn_6Au_4	Rb	Au1	In2	In1	Au2	[7]

Table 2. Experimental [2] and (calculated) crystal data for MgCo_6P_4 : $a = 6.609$ (6.56), $c = 3.380$ (3.36) Å.

Atom	site	x	y	z
Mg	$1a$	0	0	0
Co1	$3k$	0.5355 (0.535)	$2x$	$1/2$
Co2	$3j$	0.1996 (0.199)	$2x$	0
P1	$3k$	0.8151 (0.813)	$2x$	$1/2$
P2	$1c$	$1/3$	$2/3$	0

Table 3. Average Bader charges and total energy per formula unit and cohesive energies per atom for KIn_6Au_4 and RbIn_6Au_4 ($A = \text{K}, \text{Rb}$).

	Q_{In}	Q_{Au}	Q_A	$E_{\text{tot.}}(\text{eV})$	$\Delta E_{\text{at.}}(\text{eV})$
KIn_6Au_4	+0.50	−0.93	+0.72	−31.876	−0.308
RbIn_6Au_4	+0.51	−0.93	+0.66	−31.539	−0.284

Individual constituents: $E(\text{K} - \text{bcc}) = -1.01$ eV; $E(\text{Rb} - \text{bcc}) = -0.94$ eV; $E(\text{In} - \text{simple tetragonal}) = -2.44$ eV and $E(\text{Au} - \text{fcc}) = -3.21$ eV.

Table 4. Average Bader charges and total energy per formula unit and cohesive energies per atom for CeRh_6Si_4 and CeRh_6Ge_4 ($X = \text{Si}, \text{Ge}$).

	Q_{Rh}	Q_X	Q_{Ce}	$E_{\text{tot.}}(\text{eV})$	$\Delta E_{\text{at.}}(\text{eV})$
CeRh_6Si_4	−0.60	+0.54	+1.44	−82.12	−1.014
CeRh_6Ge_4	−0.58	+0.51	+1.42	−75.84	−0.777

Individual constituents: $E(\text{Ce} - \text{hex.}) = -5.71$ eV; $E(\text{Rh} - \text{fcc}) = -7.27$ eV, $E(\text{Si} - \text{fcc Blende}) = -5.41$ eV and $E(\text{Ge} - \text{fcc Blende}) = -4.49$ eV.

Fig. 1. View of the CeRh_6Ge_4 structure along the c axis. Cerium, rhodium, and germanium atoms are drawn as medium grey, black filled and open circles, respectively. The three-dimensional $[\text{Rh}_6\text{Ge}_4]$ network with Rh–Rh and Rh–Ge contacts is emphasized. The crystallographically independent rhodium and germanium sites are marked at the lower right-hand part.

Fig. 2. (color online) The crystal structure of CeRh_6Ge_4 . The $\text{Ce}@\text{Ge}_6\text{Rh}_{12}$ (blue color) and $\text{Ge1}@\text{Rh}_9$ (red color) polyhedra are emphasized. The centres of the cerium polyhedra span the hexagonal unit cell.

Fig. 3. (color online) The nature of the Rh-Rh interactions in $CeRh_6Ge_4$ from the analysis of the overlap integrals S_{ij} within the COOP scheme. Positive and negative COOP magnitudes are respectively bonding and antibonding.

Fig. 4. (color online) MgCo_6P_4 site projected density of states (top) and chemical bonding (bottom).

Fig. 5 (color online) KIn_6Au_4 site projected density of states (top) and chemical bonding (bottom).

Fig. 6. (color online) CeRh_6X_4 NSP PDOS for $\text{X} = \text{Si}$ (top) and for $\text{X} = \text{Ge}$ (bottom).

Fig. 7. (color online) UCr_6P_4 : NSP PDOS (top) and SP PDOS (bottom).