Coloring in the ZrBeSi-type structure

1 Introduction

The aristotype AlB$_2$, with an ordering of the beryllium and silicon atoms on the boron network, has been shown to allow for different colorings on the boron network along with various structural distortions, leading to a manifold of superstructures with several thousand representatives [1–4]. These superstructure variants are strictly related by group-subgroup relations [5, 6], which have been summarized in the Bärnighausen formalism [7–10].

Although several of these superstructures crystalize with the same space group type, the coloring of the Wyckoff sites with distinctly different elements and the often strong variations in the lattice parameters lead to drastic changes in the bonding patterns. The structural relationship between such compounds should be called rather isopointal than isotypic [11, 12]. The ZrBeSi type [13] is one of these superstructure variants with almost 200 representatives listed in the Pearson data base [1]. The large flexibility of this structure type with respect to the coloring of the elements and changes in the bonding pattern are discussed on the basis of the crystallographic data along with results of DFT calculations.

2 Crystal chemical considerations

In Fig. 1 we present the group-subgroup scheme for the aristotype AlB$_2$, and its ternary ordered version ZrBeSi [13]. The space group symmetry is lowered from P6/mmm to P6$_3$/mmc via a klassesgleiche transition of index 2 along with a doubling of the unit cell in c direction. This leads to a splitting of the twofold boron site into two independent twofold sites in the superstructure, enabling the ordered occupancy with beryllium and silicon. The striking feature of the ZrBeSi structure concerns the special positions for all atoms. Thus, structural variations are only possible by (i) a coloring on the three sites with different atoms and (ii) through changes of the lattice parameters a and c. All interatomic distances can be calculated directly from the lattice parameters.

An extended unit cell of the ZrBeSi structure is shown in Fig. 2. The beryllium and silicon atoms build up planar layers of condensed Be$_3$Si$_3$ hexagons. Every other layer...
of hexagons is rotated by $60^\circ$. Thus, the [BeSi] substructure of ZrBeSi corresponds to the structure of $h$-BN. The Be–Si distances of 214.9 pm are slightly longer than the sum of the covalent radii [14] of 206 pm for Be$^+$ and Si and this is indicative of covalent Be–Si bonding. Each zirconium atom has a hexagonal prismatic coordination by two Be$_3$Si$_3$ hexagons. Beryllium and silicon have trigonal prismatic zirconium coordination as emphasized in the upper right-hand part of Fig. 2. The two different Zr–Zr distances of 361.6 and 372.2 pm correspond to the edge lengths of these prisms.

A variety of different colorings has been observed for compounds with a ZrBrSi related structure. Of the many phases listed in the Pearson data base we have selected representative ones both with respect to the element coloring and the $c/a$ ratio which has large consequences on the bonding situation. These selected phases, along with their basic crystal chemical data (we mostly rely on compounds where the structure was refined from single-crystal diffractometer data) are listed in Table I and briefly discussed in the following subchapters.

### 2.1 Tetrelides

The crystal chemical discussion is started with the prototype itself. ZrBeSi [13] is a metallic compound. The zirconium and beryllium atoms can donate six valence electrons but silicon can only accept four of them, forming a Si$^4-$ Zintl anion with [Ar] configuration. The two excess electrons fill metal-centered states. Electron-precise compounds are formed if the two cations deliver four valence electrons. Typical examples are the germanides Ca$_2^+Zn^2^+Ge_4^-$ [15] or Eu$_2^+Zn^2^+Ge_4^-$ [16]. Besides the germanides also electron-precise silicides, stannides and plumbides are known and the zinc cations can be substituted by Cd$_2^+$ or Hg$_2^+$ [1].

Chemical bonding in ZrBeSi and CaZnGe is exemplarily discussed for the tetrelides below. The Zn$_3$Ge$_3$ hexagons in CaZnGe show Zn–Ge distances of 248 pm, close to the sum of the covalent radii of 247 pm [14].

The four valence electrons can also be donated by a trivalent rare earth metal and a monovalent transition metal as observed for the series of RE$^3^+Cu^2^+Si^4^-$ silicides [38]. Isostructural germanides and stannides are known. Substituting monovalent copper by beryllium leads to the two series REBeSi and REBeGe [39] which both have an excess electron donated by beryllium. These phases have been studied in detail with respect to their magnetic properties. The paramagnetic cases show ferromagnetic ordering at low temperatures with surprisingly high Curie temperatures of up to 70 K.

Not all of the tetrelide representatives keep their planar networks over the whole temperature range. For some compounds a weak puckering effect occurs along with a reduction of the space group symmetry to $P6_{3}mc$ (loss of the inversion symmetry; tendency towards the NdPtSb type). A striking example is the stannide CeCuSn [40] for which both the high- and low-temperature structures were studied from single-crystal X-ray diffraction data. The puckering leads to a weak overall increase of chemical bonding. Such a puckering effect has also been observed for $\beta$-CaZnGe [41]. Crystals of this modification were grown from a lead flux. The $\beta$-CaZnGe structure shows a layer sequence of -planar-puckered-puckered-. At this point it should be noted that $\beta$-CaZnGe is a threelayer structure ($\alpha$-CaZnGe has two layers). Thus the phase transition is a reconstructive one and both structures are
separate superstructure variants of AlB₂ [5]. The puckering effects in CeCuSn and β-CaZnGe are weak and do not lead to interlayer bonding.

Some of the rare earth based tetrelides absorb significant amounts of hydrogen. Typical examples are CeCuSiH₁.₃₃ [42] or CeCuGeH [43]. These materials were thoroughly studied with respect to changes in the magnetic ground state. For details we refer to a recent review article [44].

### 2.2 Pnictides

Most ZrBeSi-type pnictides are electron-precise compounds like Ca₂Au₃As [17] or Sr₂Ag₃Bi [18]. Such Zintl phases with closed shell anions are also formed with divalent europium [45]. With alkali metals, divalent cations are required as the third component, e.g. realized for Na⁺Be₂As⁻ [19]. Several other combinations of mono- and divalent cations are possible, e.g. K⁺/Zn²⁺ or K⁺/Hg²⁺. Interestingly, such phases have also been reported with two divalent cations; however, in order to realize an electron-precise compound, vacancy formation has been observed. Two recent examples are Sr₂(Zn₀.₅)⁺Bi⁻ and Eu₂(Zn₀.₅)⁺Bi⁻ [20]. Diffraction data gave no hint for vacancy ordering.

Exemplarily the distances for CaAuAs and NaBeAs are discussed here (vide infra). The Au₃As₃ hexagons in CaAuAs show distances of 253 pm, which are close to the sum of the covalent radii [14] of 255 pm for Au⁺As⁻. On the other hand, the Be–As distances of 221 pm in NaBeAs are longer than the sum of the covalent radii of 210 pm. This feature is addressed in the chemical bonding section.
Besides the electron-precise phases formed by the alkali, alkaline earth and divalent europium cations, a variety of phosphides and arsenides with the electron-rich transition metals have been found to form ZrBeSi-type structures. CePdP [21] and CePdAs [22] with covalently bonded [PdP] and [PdAs] networks are presented here as examples.

Similar to CeCuSn and \( \beta \)-CaZnGe discussed in the tetrelide section, also EuPtP exhibits deviations from planar [PtP] networks [46]. EuPtP shows micro-domain formation (violation of the mirror plane; puckering of the \( \text{Pt}_3\text{P}_3 \) hexagons) as a consequence of temperature-driven valence changes on going to lower temperatures.

The last example of the pnictide family concerns the metal-rich phosphide ZrNiP [23]. The nickel and phosphorus atoms build up planar Ni\(_3\)P\(_3 \) hexagons with 217 pm Ni–P distances, slightly shorter than the sum of the covalent radii of 225 pm. These covalently bonded Ni\(_3\)P\(_3 \) hexagons coordinate the zirconium atoms. The large excess of valence electrons definitely leads to metallic properties for ZrNiP.

### 2.3 Chalcogenides

Only few chalcogenides adopt the ZrBeSi-type structure. All of these compounds are electron precise. Examples selected here are K\(_{\text{+}}\)Cu\(_{\text{+}}\)Se\(_{\text{2}}\)\(^{\text{−}}\) and K\(_{\text{+}}\)Cu\(_{\text{+}}\)Te\(_{\text{2}}\)\(^{\text{−}}\) [24], Na\(_{\text{+}}\)Au\(_{\text{+}}\)Te\(_{\text{2}}\)\(^{\text{−}}\) and K\(_{\text{+}}\)Au\(_{\text{+}}\)Te\(_{\text{2}}\)\(^{\text{−}}\) [25] and the high-pressure modification HP-Rb\(_{\text{+}}\)Au\(_{\text{+}}\)Te\(_{\text{2}}\)\(^{\text{−}}\) [26]. As shown in Fig. 3, KCuGe is one of the ZrBeSi-type compounds with a large c/a ratio and well separated Cu\(_3\)Se\(_3 \) layers, without any interlayer interactions. This feature underlines the ionic description; however, these chalcogenides appear as black shiny crystals.

### 2.4 Chalcogenide hydrides and fluorides

The chalcogenides discussed in the previous chapter contain a coinage metal within the planar layers. Formation of ZrBeSi-type compounds is also observed with two different anionic moieties. This is realized in the pale bluish-gray selenide hydrides LaSeH, CeSeH, PrSeH and NdSeH [27]. The highly ionic bonding character is nicely underlined by color. Keeping the close crystal chemical relationship between hydride and fluorides in mind, it is not astonishing that LaSeF [28] has also been reported. The pale green \( \alpha \)-modification is isotypic with LaSeH. The striking difference from ZrBeSi concerns the coloring of the Wyckoff sites. The selenide anions of LaSeH and LaSeF are on the Wyckoff site 2\( \alpha \) and the lanthanum cations fill the 2\( c \) site. We thus observe planar [LaH\(_2\)]\(^{+}\) layers with 237.6 pm La–H and [LaF\(_2\)]\(^{+}\) with 243.5 pm La–F distances. These two series of compounds nicely show that their relationship with the prototype itself or the metal-rich phosphide ZrNiP is only of isopointal type since we observe a clear difference in the bonding characteristics.

### 2.5 Lithium compounds

Several lithium compounds with the ZrBeSi type have been described. Lithium shows two crystal chemically different features in these compounds. LiBC [29] and LiAuSn [30] can be considered as fully lithium-intercalated heterographites with planar [BC]\(^{−}\) and [AuSn]\(^{−}\) networks. The boride carbide has intensively been studied when searching for substitution variants of the 39 K superconductor MgB\(_2\), but no superconductivity was found for the substituted samples [47]. The ionic bonding model Li\(^{+}\)[BC]\(^{−}\) is supported by \(^7\)Li and \(^{13}\)B solid state NMR spectra [29]. LiBC shows poor performance as a battery material, and the lithium ions show only moderate mobility on the NMR timescale.

Early electronic structure calculations on LiAuSn underlined the two-dimensional character of the [AuSn]...
2.6 Intermetallic compounds

Purely intermetallic phases are no longer electron precise. The examples to be considered here are NbRhGa [33], TiPtAl [34], TiAuAl [35], TiPtGa [36], and TiCuSn [37], which are related to the phases discussed above. The main group elements form the planar networks together with the AlB2 type. The lattice parameters c range from 1199 to 1295 pm. Since the interatomic distances in the ZrBeSi structure solely depend on the lattice parameters, it is evident, that the trigonal prisms are much too high and most interatomic distances are physically unreasonably long. Either these compounds have a sequence of three layers or there is a strong puckering effect. These phases deserve a precise investigation based on single-crystal data.

The striking difference with respect to the electron-precise phases discussed above concerns the c/a ratios of the unit cells. For our examples NbRhGa and TiPtGa, the trigonal prisms around the rhodium (platinum) and gallium atoms are strongly compressed (see the values in Table 1), leading to substantial Nb–Nb and Ti–Ti bonding along the c axis, while the interactions in the ab plane are much weaker. This bonding situation is similar to that in many NiAs-type phases with compressed prisms, which show enhanced electrical and thermal conductivity in c direction. Within the planar polyanionic layers one observes Rh–Ga and Pt–Ga distances of 256.7 and 252.5 pm, which are both close to the sum of the covalent radii (250 pm for Rh+Ga and 254 pm for Pt+Ga). We thus observe an overall increase of covalent and metallic bonding in these phases.

3 DFT calculations

The crystal chemical discussion impressively showed the large flexibility of the ZrBeSi structure with respect to coloring and variability in chemical bonding, ranging from pure salts via electron-precise Zintl phases to intermetallic compounds. This is addressed here in more detail for selected compounds based on calculations within the quantum density functional theory (DFT) [50, 51] framework.

3.1 Technical details

Within DFT plane wave calculations were carried out to optimize atomic positions and lattice parameters using the VASP code [52, 53]. The geometry optimization, leading to the ground state configurations, provides for each composition minimal interatomic forces and zero strains. Calculations were performed considering total spin configurations. The projector augmented wave (PAW) method [53] was used with potentials built within the generalized gradient approximation (GGA) for an account of the effects of exchange and correlation [54, 55]. In so far that the atoms are all at special Wyckoff positions within the ZrBeSi-type structure adopted by the equiatomic compounds under consideration, only the hexagonal lattice parameters a and c underwent changes upon iterative calculations searching for minimal configuration. Within the GGA those changes were systematically found to be 2–5% larger than the experimental values. Such results allowed analyzing the charge density to extract the magnitude of charge transfers inferred from the approach by Bader in the framework of the Atoms in Molecules AIM theory [56]. In short,
Bader devised an intuitive way of splitting molecules into atoms as based purely on the electronic charge density. Typically in chemical compounds, the charge density reaches a minimum between atoms and this is a natural region to separate them from each other. Such an analysis can be useful when trends between similar compounds are examined, but it is not a tool for evaluating absolute ionizations. Electron localization mapping is illustrated for a few representative compounds with electron localization (EL) using the ELF function introduced by Becke and Edgecomb [57] as based on the kinetic energy in which the Pauli Exclusion Principle is included. ELF is a normalized function, i.e. $0 < \text{ELF} < 1$ with $\text{ELF} = (1 + \chi_{\sigma})^{-1}$. In this expression the ratio $\chi_{\sigma} = D_{\sigma}/D_{\sigma}^{0}$, where $D_{\sigma} = r_\sigma^{-\frac{1}{2}}(\nabla \rho_{\sigma})/\rho_{\sigma}$ and $D_{\sigma}^{0} = 3/5 \pi^{2} \rho_{\sigma}^{\frac{5}{3}}$ correspond respectively to a measure of Pauli repulsion ($D_{\sigma}$) of the actual system and to the free-electron gas repulsion ($D_{\sigma}^{0}$), and $r_\sigma$ is the kinetic energy density.

Detailed calculations of the electronic structure and the chemical bonding properties were carried out using the full-potential augmented spherical wave (ASW) method in its scalar-relativistic implementation [58, 59] with effects of exchange-correlation treated within GGA [55]. In the ASW method, the wave function is expanded in atom-centered augmented spherical waves, which are Hankel functions and numerical solutions of Schrödinger’s equation, respectively, outside and inside the so-called augmentation spheres. In order to optimize the basis set, additional augmented spherical waves were placed at carefully selected interstitial sites. In the minimal ASW basis set, the outermost shells were explicitly used to represent the valence states with partial waves up to $l_{\text{max}} + 1$ for the different atomic species where $l_{\text{max}}$ is the maximum secondary quantum number, e.g. $l_{\text{max}} = 2$ for a transition metal and $l_{\text{max}} = 1$ for fluorine.

Self-consistency was achieved when the variation of the atomic charges was smaller than $10^{-8}$ electrons and the variation of the total energy was smaller than $10^{-7}$ eV. Further within the crystal orbital overlap population (COOP) approach of Hoffmann [60], the ASW method implements the chemical bonding for pair interactions provided as based on the overlap integral $S_{\langle i,j \rangle}$ designating two chemical species. In so far that COOPs are overlap integral weighted DOS, we only illustrate DOS and COOP exemplarily for two compounds (chapter 3.4).

### 3.2 Charge transfer trends

Based on the results obtained from calculations at a high resolution of the Brillouin zone integration, the calculated charge density is analyzed based on the Bader AIM theory [56].

Table 2 presents (per class of compounds) the calculated charge transfer $Q$ at each of the three crystallographic sites in these equiatomic $AX$ compounds. As a general trend, the $A$ atom is most electropositive and loses electrons to the $T$ and $X$ atoms. As already stated above, the established trends do not constitute a tool for evaluating absolute ionizations; i.e. only relative trends are discussed. This is illustrated starting with the tetrelides ZrBeSi and CaZnGe where both Zr and Ca lose $\sim$1.4 electrons, i.e. far from full ionization (Ca$^{2+}$ for instance). Thus, zirconium is also close to divalent in character. More significant changes are observed for the [TX] substructures where Be loses more electrons to X (Si) characterizing ZrBeSi as more ionic than CaZnGe.

For the pnictide family, the electronegativity of the $T$ element plays an important role. In CePdP and ZrNiP both Pd and Ni are negatively charged. This is in line with the course of the Pauling electronegativities: $\text{EN}_{\text{pd}} = 2.20$ and $\text{EN}_{\text{ni}} = 1.91$ [14]. Together with the P ($\text{EN}_{\text{p}} = 2.19$) atoms the two transition metals charge-balance the $A$ substructure. Similar situation is observed for CaAuAs with highly electronegative gold ($\text{EN}_{\text{au}} = 2.54$) carrying a charge of $-0.79$. This data is in good agreement with a recent study involving Löwdin charges: Ca $+1.47$, Au $-0.63$ and As $-0.84$ [61]. Auride character has experimentally been

<table>
<thead>
<tr>
<th>Compound</th>
<th>$Q (A)$</th>
<th>$Q (T)$</th>
<th>$Q (X)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrelides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrBeSi</td>
<td>1.37</td>
<td>0.95</td>
<td>-2.32</td>
</tr>
<tr>
<td>CaZnGe</td>
<td>1.37</td>
<td>-0.26</td>
<td>-1.11</td>
</tr>
<tr>
<td>Pnictides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaAuAs</td>
<td>1.45</td>
<td>-0.79</td>
<td>-0.66</td>
</tr>
<tr>
<td>NaBeAs</td>
<td>0.86</td>
<td>1.24</td>
<td>-2.10</td>
</tr>
<tr>
<td>CePdP</td>
<td>1.49</td>
<td>-0.63</td>
<td>-0.86</td>
</tr>
<tr>
<td>ZrNiP</td>
<td>1.59</td>
<td>-0.38</td>
<td>-1.21</td>
</tr>
<tr>
<td>Chalcogenides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCuSe</td>
<td>0.76</td>
<td>0.22</td>
<td>-0.98</td>
</tr>
<tr>
<td>Chalcogenide hydrides and fluorides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaSeH</td>
<td>1.22</td>
<td>-0.99</td>
<td>-0.23</td>
</tr>
<tr>
<td>LaSeF</td>
<td>1.78</td>
<td>-0.95</td>
<td>-0.83</td>
</tr>
<tr>
<td>Lithium compounds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiBC</td>
<td>0.86</td>
<td>0.10</td>
<td>-1.96</td>
</tr>
<tr>
<td>LiAuSn</td>
<td>0.86</td>
<td>-1.12</td>
<td>0.26</td>
</tr>
<tr>
<td>SrLiP</td>
<td>1.22</td>
<td>0.86</td>
<td>-2.08</td>
</tr>
<tr>
<td>Intermetallics</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NbRhGa</td>
<td>0.88</td>
<td>-0.78</td>
<td>-0.10</td>
</tr>
<tr>
<td>TiPtGa</td>
<td>1.69</td>
<td>-1.82</td>
<td>0.13</td>
</tr>
</tbody>
</table>
observed for CaAuX (X = Al, Ga, In) and BaAuGa from Au 4f photoemission spectra [62], underpinning the present calculations.

At this point it becomes interesting to examine concomitantly CaZnGe which exhibits a slightly negative charge on Zn of −0.26. As discussed above, both CaAuAs and CaZnGe can be described as electron-precise Zintl phases expressed formally as Ca\^{2+}Au\^{+}As\^{3−} and Ca\^{2+}Zn\^{2+}Ge\^{4−}; however, these limiting formulations do not reflect the real charge exchange. Nevertheless, if we keep the electron affinities in mind (in units of kJ mol\(^{-1}\) [14]: Ca −186, Au +222.8, As, +78, Zn +9 and Ge +116) we can understand the auride character for CaAuAs and the slightly negative charge for zinc in CaZnGe. Negative Bader charges were most recently also observed for CaMgZn\(_{10}\), CaZn\(_{11}\), CaMgZn, and Ca\(_2\)Mg\(_6\)Zn\(_{15}\) [63], again in agreement with the course of the electron affinities: Ca −186, Mg −21 and Zn +9 [14]. These results are further illustrated with a comparative study of the DOS and COOP in the next sections.

KCuSe, as a representative of the chalcogenides, shows regular trends of positively charged K with a charge close to unity and with \(E_{\text{N}}_{\text{Cu}} = 1.90 < E_{\text{N}}_{\text{Se}} = 2.55\) indicating a charge transfer from Cu to Se. For LaSeF and LaSeH we observe a larger charge transfer towards fluorine (\(E_{\text{N}}_{\text{H}} = 2.2\) vs. \(E_{\text{N}}_{\text{F}} = 3.98\)), and this is compensated by lanthanum.

The lithium-based compounds were studied with 1s\(^2\) as core states explicitly accounted for in the electron configuration; otherwise with only one valence electron ionic behavior would be much higher (a comparable situation occurs for magnesium hydride, where the realistic charge of −0.82 is obtained for hydrogen if one uses 3s\(^2\) and 2p\(^6\) as half-core states for magnesium). The results systematically show Li\(^{0.86}\) and larger changes on the other constituents. In LiAuSn, we also accounted for Sn full 3d\(^{10}\) states in the basis set. With Au being more electronegative than Sn (\(E_{\text{N}}_{\text{Au}} = 2.54\) vs. \(E_{\text{N}}_{\text{Sn}} = 1.96\)), it gains 1.12 electrons while Sn loses much less charge (0.26). In SrLiP both Sr and Li transfer electron density to P as expected.

Finally considering the intermetallic compound NbRhGa, major charge transfer is found between Nb and Rh with Nb→Rh (\(E_{\text{N}}_{\text{Nb}} = 1.6\) vs. \(E_{\text{N}}_{\text{Rh}} = 2.28\)). Ga with intermediate magnitude of electronegativity (\(E_{\text{N}}_{\text{Ga}} = 1.81\)) shows little departure from neutrality.

### 3.3 Electron localization function mapping

The charge changes translating the anionic into the cationic substructures can be further illustrated through ELF mapping. Taking the aristotype ZrBeSi as an example, we show in Fig. 4 the 3D and 2D ELF surfaces over four adjacent cells. For the normalized ELF function, i.e. \(0 < \text{ELF} < 1\), the color code is ELF = 0, no localization; blue areas; full localization; ELF ~1 with red areas and green areas for ELF ~1/2, i.e. free electron-like behavior.
At the basal plane where the Zr atoms are found there is zero localization (blue areas) in the immediate vicinity of positively ionized Zr, but green-like areas appear between them. This is in agreement with a metallic behavior of the compound as observed from the DOS with finite magnitudes at $E_F$. Interesting features appear from the 3D ELF surfaces around Si, while no such envelopes can be identified around Be. This complies with the $Q$ magnitude observed (Table 2): $Q_{Zr} = 1.37$, $Q_{Be} = 0.95$ and $Q_{Si} = -2.32$. The 3D ELF envelopes show a three-fold structure with $sp^2$-like hybridization of the atoms. This is further stressed in the middle part of Fig. 4 where planes are shown together with the 3D ELF crossing the Be–Si bond. Clearly red areas with strong electron localization show up only in the vicinity of Si, and free electron-like behavior is found at the Be sites. The three 3D ELF lobes point to Be just like in a honeycomb lattice.

Exemplarily we now turn to the cases of CaZnGe and CaAuAs. Figure 5 shows the ELF slices at $z = 1/4$ and along a diagonal 110 plane for both compounds. While green areas point to free-electron like localization around Zn, larger localization can be seen with deep yellow ELF around Au which carries a larger magnitude of negative charge. Largest localizations are found with red areas surrounding Ge and As. This is observed for both projection directions. Ca with blue areas pointing to no electron localization in the immediate vicinity of blue spheres is observed to expand into free electron-like nature in the interatomic space in accordance with the metallic behavior of both compounds. These representations agree well with the Bader charges. Note the similarities of Ge with Si (in ZrBeSi) which are isoelectronic.

### 3.4 Site-projected electron density of states

A full account of the electronic structure was obtained with the all electrons scalar relativistic ASW method presented above. For a selected number of compounds, Fig. 6 shows the site-projected DOS (PDOS). The energy reference in the DOS plots is with respect to the Fermi level $E_F$ or the top of the valence band $E_V$ in some semi-conducting/insulating compounds. All calculations assume non-spin-polarized (NSP) magnetic configurations. Only for CePdP a spin-polarized (SP) configuration was considered herein.

Starting with ZrBeSi for which a full analysis of the ELF was presented in Fig. 4, the itinerant character of the electrons is illustrated by the green areas in the ELF slice crossing the Be–Si plane. Also there is a close resemblance of the PDOS of these coplanar elements in two energy ranges: from $-12$ to $-8$ eV for $s$-like states showing similar $s$ PDOS for all three constituents, and from $-7$ eV up to $E_F$ where $p$-like states are found with similar skylines not only for Be and Si but also for Zr whose $4d$ states are centered above $E_F$ within the conduction band. On the other side, KCuSe has a full valence band and the energy reference is with respect to $E_F$. Indeed a gap of 0.5 eV separates the valence band (VB) from the empty conduction band (CB). From Table 2 there is approximately $\pm 1$ electron exchange between the K/Cu cationic and the Se anionic substructure, whence the semiconducting behavior.

In contrast to both ZrBeSi (itinerant-like behavior of electrons at $E_F$) and KCuSe (semiconductor), CePdP shows intense Ce PDOS at $E_F$. This corresponds to well-localized $4f$ states which contain unpaired $f$ electrons. Such a fingerprint is a clear signature of an electronic instability and there should occur energy stabilization by letting spin-polarization occur. The VB is dominated by filled $4d^{10}$ Pd electrons, which show a skyline similar to $Pp$ between $-6$ and $-1$ eV. The $P$-s states are well identified at $-11$ eV.
Fig. 6: Site-projected density of states (DOS) plots of selected representatives of ZrBeSi-related compounds.
Subsequent SP calculations indeed led to the onset of a small but finite magnetization on Ce-4f with a magnitude of 0.6 μB. Note that SP calculations implicitly involve a ferromagnetic configuration. This is perfectly in line with the experimental magnetic data, which show a Curie temperature of 5.2 K [44, 64].

LiBC which also shows ±Q ~ 2 (Li: +0.86, B: +1.10, C: −1.96) has a band gap of ~0.5 eV. The VB is also divided in two parts, s-like between −15 and −10 eV and p-like up to E\textsubscript{V}. The skyline of all constituents’ PDOS is an indication of chemical bonding between all three elements and more specifically between boron and carbon within the [BC]\textsuperscript{−} polyanion. The same situation arises for SrLiP with an exchange of two electrons between Sr and Li on one hand and P on the other hand. This leads to semiconducting behavior, in good agreement with a recent study by Benahmed et al. [65].

Lastly, for NbRhGa there is a metallic behavior at E\textsubscript{F} materialized by itinerant low intensity PDOS arising from all constituents which quantum-mix their valence states. Note that for the counterpart of Rh, which is in the 2nd half of the 4d metals with its states within the VB, namely Nb, an early element of the 4d metals, the 4d band is centered above E\textsubscript{F} within the empty conduction band, so that its itinerant part mixes with Rh and Ga.

Again, we focus in more detail on the DOS (Fig. 7 left) and COOP (Fig. 7 right) plots of CaAuAs and CaZnGe, in order to underline the course of the Bader charges discussed above. Both compounds are close to insulators, what complies with the picture of a Zintl precise electron partitioning. In CaZnGe, the Fermi level is at a deep minimum whereas in CaAuAs there is a gap of ~1 eV and E\textsubscript{F} is now E\textsubscript{V} designating here the bottom of the conduction band. An in-depth study, characterizing CaAuAs as a nodal-line semimetal was recently published by Singh et al. [66], focusing on the topological band structure.

The low-energy filled d states of Zn and Au are centered within the valence band at −8 and −6 eV, respectively. However, both compounds exhibit a low intensity broad PDOS extending over the VB, signaling chemical bonding with the valence states of the other constituents. The bonding is illustrated through COOP plots on the

![Fig. 7: Site-projected density of states (DOS) plots and COOP diagrams for CaZnGe (top) and CaAuAs (bottom).](image-url)
right-hand panels of Fig. 7. They show pair interactions for the different constituents.

In spite of the equal distances \( A-X = A-T \) (Table 1; restricted by symmetry) the Ca valence states have clearly much larger bonding with Ge and As than with Zn and Au. This arises from the electronic configurations of the counter ions: \( \text{nd}^{10} \) for Zn and Au whereas Ge and As have unsaturated external \( p \) shells. The corresponding COOPs are large and spread out in the energy range between \(-4 \) eV and \( E_i \) (\( E_r \)).

The in plane Au–As and Zn–Ge COOPs show non-negligible \( d-p \) bonding at the energy positions of the Zn and Au \( d \)-states with positive (bonding) COOP intensities throughout the VB of CaZnGe whereas they become significantly antibonding in the case of CaAuAs. Thus, Zn–Ge bonding is mainly of \( s-p \) character, opposite to Au–As which is more of \( d-p \) character. BaZnSn shows a similar fingerprint [67].

### 3.5 Structural stability of ZrBeSi

The elastic properties of a compound are determined by performing finite distortions of the lattice and deriving the elastic constants from the strain-stress relationship. In tetragonal and hexagonal symmetries there are six independent elastic stiffness constants \( C_{11} \), \( C_{12} \), \( C_{13} \), \( C_{33} \), \( C_{44} \), \( C_{66} \). The samples of most compounds investigated in this context were polycrystalline (randomly oriented crystalline grains) so that on a large scale, such materials can be considered as statistically isotropic. They are then described by the bulk modulus \( B \) and the shear modulus \( G \), which may be obtained by averaging the single-crystal elastic constants.

The most widely used averaging method of the elastic stiffness constants is the method of Voigt [68, 69] based on a uniform strain. In ZrBeSi the calculated elastic constants are in units of GPa:

\[
\begin{align*}
C_{11} &= C_{22} = 301; \\
C_{12} &= 65; \\
C_{13} &= 73; \\
C_{33} &= 230; \\
C_{44} &= 118; \\
C_{66} &= 133.
\end{align*}
\]

All \( C_{ij} \) values are positive and their combinations: \( C_{11} > C_{12} \) and \( (C_{11} + C_{12})C_{33} > 2C_{13}^2 \) obey the rules pertaining the mechanical stability of a compound. Focusing on \( C_{ij} \) translating stresses along the three orthogonal axes, it can be observed that \( C_{11} = C_{33} \) (coupled by symmetry) are larger than \( C_{13} \) (along the \( c \) axis). This is explained by the planar hexagonal [BeSi] network (Fig. 2), leading to a hardness orthogonally to the \( c \) axis and a softness one along \( c \).

The bulk \( (B_v) \) and shear \( (G_v) \) modules following Voigt are:

\[
B_v = 1/9 \left( 2(C_{11} + C_{12}) + 4C_{13} + C_{33} \right)
\]

and

\[
G_v = 1/30 \left( 12C_{44} + 12C_{66} + C_{11} + C_{12} + 2C_{33} - 4C_{13} \right)
\]

Interestingly the numerical calculations provide equal \( B_v \) and \( G_v = 139 \) GPa.

Whereas the magnitude of the bulk modulus \( B_v \) is much lower than the one for the hardest material, i.e. diamond with \( B = \sim 450 \) GPa, \( G_v \) defines the rigidity of the material. A relationship between the two properties was established by Pugh with the \( G_v/B_v \) ratio [70]. This ratio is an indicator of brittleness or ductility for \( G_v/B_v > 0.5 \) and \( G_v/B_v < 0.5 \), respectively. Here the ratio close to one characterizes ZrBeSi as extremely brittle. Unfortunately no mechanical data have been published in the original work on ZrBeSi [13]. Nevertheless, most of the ZrBeSi-type phases have been described as brittle solids.

### 4 Conclusions

The present work gives an overview on the coloring variants of the ZrBeSi related phases. This family of compounds covers the broad range from electron-precise salt-like materials like the selenide hydride LaSeH and the selenide fluoride LaSeF via typical Zintl phases like \( \text{Sr}^2\text{Li}^3\text{P}^5 \) or \( \text{Na}^+\text{Be}^3\text{As}^5 \) to purely intermetallic phases like NbRhGa. This highly symmetric structure type (space group \( P6_3/mmc \)) contains three crystallographically independent sites, all on special Wyckoff positions. Thus, only the lattice parameters \( a \) and \( c \) are variables. Nevertheless, this already allows for extreme flexibility for the atomic arrangements, leading to the broad variations of bonding (semiconductors/metals). In view of these differences, not all phases in the Pearson data base [1] listed under the prototype ZrBeSi are isotypic; several are just isopointal [11, 12].

While the present study focused on the crystal chemical classification and the bonding peculiarities of the complete series of ZrBeSi related compounds, recent investigations have also focused on some of these materials with respect to their nature of three-dimensional topological Dirac semimetals [71], one of the current research branches in solid state physics.

**Acknowledgements:** Calculation facilities were provided by LGU Center for Scientific Computing.
References


