Infinite linear chains of Sb atoms in the novel metal-rich polyantimonides $Zr_{7.5}V_{5.5}Sb_{10}$ and $Zr_{6.5}V_{6.5}Sb_{10}$

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The structures of the title compounds exhibit short Sb–Sb bonds besides a multitude of bonding M–M interactions, *i.e.* the M atoms (Zr and V) in low valent states.

Partial electron transfer from the anionic to the cationic component has been used for a variety of so-called '*chimie-douce*' reactions.[1] Whereas the distances between the tellurium atoms decrease in the structures of the ditellurides from $ZrTe_2$ to $PdTe_2$ with increasing electronegativity of the metal atoms, the systematics of the Sb–Sb distances of the monoantimonides is less clear.

No Sb–Sb contacts < 350 pm occur in the structures of many monoantimonides of valence-electron poor transition metals like ScSb[2] and YSb[3] (both NaCl type), TiSb,[4] VSb[5] and NbSb[6] (all NiAs type). This may be considered as a hint to completely reduced Sb(-III). On the other hand, the structure of ZrSb[7] consists in part of puckered layers containing Sb_6 units with Sb–Sb distances of *ca.* 325 pm, which point to weak bonding interactions. This was the motivation to study Zr-rich antimonides. Here, the most metal-rich polyantimonides are presented, whose structures exhibit Sb–Sb bonds besides bonding metal–metal interactions. This observation is in contrast to related metal-rich tellurides[8] and arsenides[9] where neither Te–Te nor As–As bonds were found.

The isostructural pnictides $Zr_{7.5}V_{5.5}Sb_{10}$ and $Zr_{6.5}V_{6.5}Sb_{10}$[10] were synthesized by arc-melting of stoichiometric cold-pressed mixtures of Zr, V, and previously prepared $ZrSb_2$.[11] The metal sites are in part statistically mixed occupied by Zr and V in different ratios. The configurational entropy provides a significant contribution to the stability of these phases, which decompose during annealing at lower temperatures, namely at 900 and 1100 °C. The metal sites may be devided into two classes: the seven independent sites of the first class (white circles in Fig. 1) consist mainly of Zr atoms and form alternating triangles and rectangles parallel to the *b* axis. Five of these positions are surrounded by seven Sb atoms forming distorted pentagonal bipyramides, whereas the other two are located in pentagonal Sb_6 pyramides. The three independent positions of the second class (black circles in Fig. 1, mainly V atoms) are situated in distorted Sb_6 octahedra and Sb_5 square prisms, respectively.

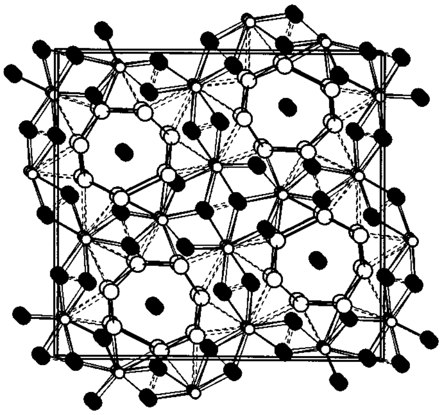

Fig. 1 Projection of the structure of $Zr_{7.5}V_{5.5}Sb_{10}$ along [010]. Large white circles: M atoms of class I (mainly Zr); small white: M atoms of class II (mainly V); medium black: Sb.

Considering to a first approximation the sites of the first class solely as Zr sites and those of the second class as V sites, corresponding to a hypothetical '$Zr_7V_6Sb_{10}$', the Zr/V ratio per metal site decreases with increasing total M–Sb Pauling bond order, calculated with r_{Zr} = 145 pm, r_V = 122 pm.[12] It is concluded that the site preferences of Zr and V are mainly dominated by the different radii of the M atoms rather than by the different number of valence electrons which should influence basically only the metal–metal interactions.[13] Given the fact that $Zr_{7.7}V_{5.3}Sb_{10}$ and $Zr_{6.5}V_{6.5}Sb_{10}$ crystallize in a new structure type in addition to the occurrence of differential fractional site occupancies, these phases may be classified as typical DFSO stabilized materials,[14] being the first with the very different metal atoms, Zr and V. However, only three ($Zr_{6.5}V_{6.5}Sb_{10}$) or four ($Zr_{7.5}V_{5.5}Sb_{10}$) of the ten M sites show mixed Zr/V occupancies. On the other hand, complete ordering of the Zr and V atoms is observed in the structure of $Zr_2V_6Sb_9$.[15]

The metal atoms are interconnected *via* short metal–metal bonds with lengths between 260 and 310 pm. The majority of these interactions are found between atoms of class II parallel to [010] and between the atoms of the classes I and II, whereas only one of these relatively short bonds connects two atoms of class I, being situated in the *ac* plane [thick line in Fig. 2(a)]. The atoms of the first class form channels which include linear chains of Sb atoms with short alternating Sb–Sb distances of 280 and 288 pm for $Zr_{7.5}V_{5.5}Sb_{10}$ ($Zr_{6.5}V_{6.5}Sb_{10}$: 281 and 288 pm). It is interesting that the surrounding electropositive Zr

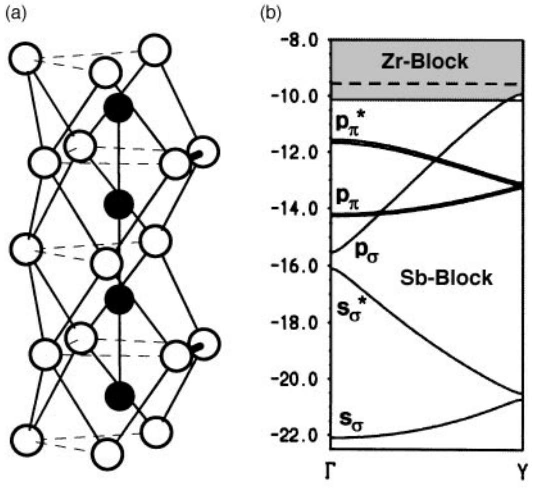

Fig. 2 (a) Part of the infinite $(Zr, V)_7Sb_2$ chain. Thick solid line between M atoms: distance d = 305 pm, thinner lines: 350 pm < d < 370 pm; dashed lines: 380 pm < d < 430 pm. (b) Schematic band structure of an infinite Zr_7Sb_2 unit.

atoms use some electrons for Zr–Zr bonds instead of reducing antimony to Sb(-III). Other Sb–Sb distances in this structure range from 330 to 350 pm (dashed lines in Fig. 1) which is comparable to the second shortest Sb–Sb bonds in elemental antimony (336 pm). Whereas the bonding character of these interactions remains questionable, the shorter distances, being shorter than in elemental antimony (291 pm), may be compared to the lengths of two-electron–two-center bonds found in other polyantimonides, namely in KSb (283 and 285 pm),[16] cyclo-Sb_5^{5-} (between 281 and 291 pm),[17] and Sb_{11}^{3-} (between 276 and 285 pm).[18]

However, the linearity of the Sb chain stands against two-electron–two-center bonds, as can be derived from a comparison with the zigzag Sb(-I) chains in KSb or the Te chains in elemental tellurium. In order to obtain more information about bonding in the Sb chain, the band structure of an infinite Zr_7Sb_2 chain with the atomic positions of the structure of $Zr_{7.5}V_{5.5}Sb_{10}$ (Fig. 2) was calculated using an extended Hückel approximation[19] with parameters listed previously.[15] As a consequence of the Peierls distortion, a gap occurs between the highly disperse p_σ and the p_σ* band of the Sb atoms. With the exception of the p_σ* band, all p states of the Sb atoms are located well below the Zr centered states [Fig. 2(b)]. Since the Zr states are partially occupied because of the bonding Zr–Zr interactions, seven bands of the two Sb atoms of the unit are completely filled, *i.e.* with two electrons per band. This leads to a formal consideration of these Sb atoms being Sb^{2-} which form (delocalized) one-electron–two-center Sb–Sb σ bonds. The latter gives a straightforward explanation for the linearity of the ${}^{1}_{\infty}[Sb^{2-}]$ chain, but not for the short bond lengths. The shortness of the Sb–Sb bonds is most likely a consequence of matrix effects, enabling a relatively short *b* axis and thus strong bonding metal–metal interactions parallel to the *b* axis. In a crude approximation, the formal electron counting schemes (ignoring the Sb–Sb interactions > 330 pm) of $(Zr^{4+})_{7.5}(V^{5+})_{5.5}(Sb^{2-})_2(Sb^{3-})_8(e^-)_{29.5}$ and $(Zr^{4+})_{6.5}(V^{5+})_{6.5}(Sb^{2-})_2(Sb^{3-})_8(e^-)_{30.5}$ show a multitude of electrons (*ca.* 2.3 per M atom) being available for (delocalized) M–M bonds and result in a reasonable averaged oxidation state of −2.8 for the Sb atoms.

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10 *Crystal data* (IPDS, Stoe, T = 293 K): $Zr_{7.5}V_{5.5}Sb_{10}$: M = 2182 orthorhombic, space group *Pnma*; a = 1871.6(2), b = 567.22(6), c = 1764.9(2) pm; Z = 4, μ = 20.7 mm^{-1}, 2681 independent reflections; $R(F)$ = 0.036, $R_w(F^2)$ = 0.074 for 1069 observed reflections [$I > 2\sigma(I)$]. $Zr_{6.5}V_{6.5}Sb_{10}$: M = 2142 orthorhombic, space group *Pnma*, a = 1866.7(3), b = 569.09(7), c = 1753.7(2) pm, Z = 4, μ = 20.7 mm^{-1}, 2433 independent reflections; $R(F)$ = 0.060, $R_w(F^2)$ = 0.111 for 575 observed reflections [$I > 2\sigma(I)$]. CCDC 182/1007.

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