

Figure 2. Chains of *cis*-edge-sharing  $\text{IO}_6$  octahedra.

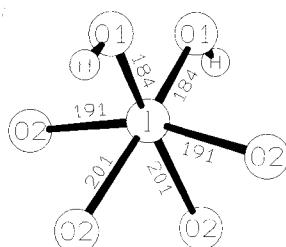


Figure 3.  $\text{IO}_6$  octahedron; distances are given in pm.

The structural analogy to many transition metal tetrahalides, as indicated by the presence of chains of *cis*-edge-sharing octahedra, also extends on the arrangement of these structural units relative to each other. When considering the I–O substructure, isotyprism to uranium tetraiodide becomes evident, that is, the oxygen atoms form a hexagonal close packing with the iodine atoms occupying a quarter of the octahedral holes.

Every polymeric chain is connected to four adjacent chains through hydrogen bonds (Figure 4;  $d(\text{O} \cdots \text{O})$  269(2) pm,

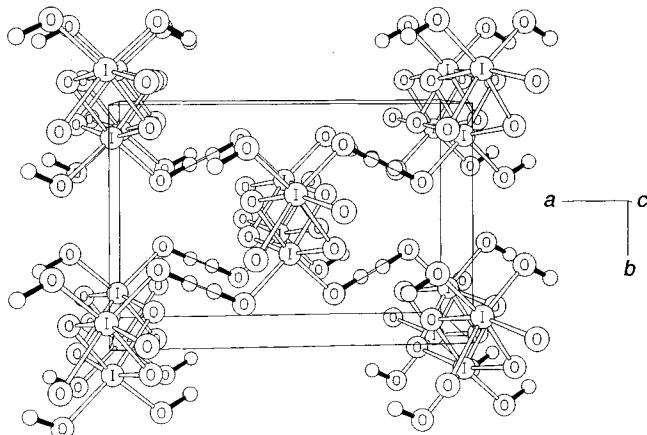


Figure 4. Connectivities between the chains through hydrogen bridges.

$d(\text{O}-\text{H})$  101(3) pm,  $d(\text{O} \cdots \text{H})$  169(3) pm,  $\angle \text{I}-\text{O}-\text{H}$  112(1) $^\circ$ ,  $\angle \text{O}-\text{H} \cdots \text{O}$  176(1) $^\circ$ ). The hydrogen atoms are disordered in a double potential between the terminal oxygen atoms. This is frequently observed for linear hydrogen bonds between neutral molecules, such as in the Ih modification of ice.<sup>[7]</sup>

Until now no periodate derived from the structure of  $\text{HIO}_4$ —that is, built up by polymeric iodine–oxygen chains—is known. The structure of  $\text{HIO}_4$  raises questions about the linkage of the iodine–oxygen polyhedra in oligomeric periodic acids. However, the crystal structure of  $\text{H}_7\text{I}_3\text{O}_{14}$  does not show any new type of catenation, because this compound exists in the solid state as a stoichiometric phase containing orthoperiodic and metaperiodic acids according to the formula  $\text{H}_5\text{IO}_6 \cdot 2\text{HIO}_4$ .<sup>[8]</sup>

## Experimental Section

$\text{HIO}_4$ : Oleum (25%, 15 mL) was slowly added to a solution of  $\text{H}_5\text{IO}_6$  (3 g) in concd  $\text{H}_2\text{SO}_4$  (40 g) at 50°C until an insoluble precipitate appeared. Upon standing for 12 h at 50°C a voluminous precipitate separated, which was isolated by filtration under an inert-gas atmosphere. It was treated with concd  $\text{H}_2\text{SO}_4$  (15 mL), washed with trifluoroacetic acid (5 × 15 mL) to remove traces of  $\text{H}_2\text{SO}_4$ , and finally dried in vacuo. Elemental analysis: iodine: 65.5% (calcd 66.1%), active oxygen: 27.9% (calcd 29.2%), sulfate: not detected.

Structure determination of  $\text{HIO}_4$ : After indexing [9] the X-ray powder diagram (Stoe Stadi P,  $\text{CuK}\alpha$  radiation,  $\lambda = 154.051$  pm) on the basis of a monoclinic system ( $a = 936.88(5)$ ,  $b = 629.59(4)$ ,  $c = 495.30(3)$  pm;  $\beta = 94.953(3)^\circ$ ,  $Cc$  (no. 9) and  $C2/c$  (no. 15) were considered as possible space groups from the systematic absences. In both space groups the iodine- and oxygen-atom positions were determined with direct methods [10], but a crystal-chemically consistent refinement (156 reflections, 30 parameters,  $R = 0.0617$ ,  $R_{wp} = 0.219$ ,  $R_F = 0.0522$  [11]) could only be achieved in the space group  $C2/c$ . The hydrogen bridges and, thus, the approximate positions of the hydrogen atoms were derived from crystal-chemical considerations. To verify these results optimized structure models (space group  $C2/c$  with disordered H atoms and  $Cc$  with no disordering of H atoms) were refined on the basis of neutron diffraction data ( $\lambda$  determined to 112.704 pm [11], two-circle neutron diffractometer SV7 equipped with a linear position-sensitive JULIOS detector from the Mineralogisches Institut der Universität Bonn at the reactor FRJ2 of the KFA Jülich). The model with space group  $C2/c$  was unambiguously the correct one ( $a = 936.60(18)$ ,  $b = 628.86(13)$ ,  $c = 495.75(19)$  pm;  $\beta = 94.890(15)^\circ$ ; 282 reflections, 27 parameters,  $R = 0.0185$ ,  $R_{wp} = 0.336$ ,  $R_F = 0.21$  [11]).

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- [1] A. F. Holleman, E. Wiberg, N. Wiberg, *Lehrbuch der Anorganischen Chemie*, 10th ed., deGruyter, Berlin, 1995, pp. 485–488.
- [2] Y. D. Feikema, *Acta Crystallogr.* 1961, **14**, 315–316; *ibid.* 1966, **20**, 765–769.
- [3] H. Siebert, *Fortschr. Chem. Forsch.* 1967, **8**, 470–492.
- [4] H. Siebert, U. Woerner, *Z. Anorg. Allg. Chem.* 1977, **429**, 34–38.
- [5] L. Pačesová, Z. Hauptman, *Z. Anorg. Allg. Chem.* 1963, **325**, 325–333.
- [6] J. H. Levy, J. C. Taylor, A. B. Waugh, *Inorg. Chem.* 1980, **19**, 672–674.
- [7] S. W. Peterson, H. A. Levy, *Acta Crystallogr.* 1957, **10**, 70–76.
- [8] T. Kraft, Dissertation, Universität Bonn (Germany), 1995.
- [9] P.-E. Werner, L. Eriksson, M. Westdahl, *J. Appl. Crystallogr.* 1985, **18**, 367–370.
- [10] Stoe & Cie, CSD V4.10, Darmstadt (Germany), 1991.
- [11] J. Rodriguez-Carvajal, *Fullprof*, Laboratoire Leon Brillouin (CEA-CNRS), Saclay, 1995.

## $\text{Ge}_9^{4-}$ : A Deltahedral Zintl Ion Now Made in the Solid-State\*\*

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All known main group deltahedral clusters are made either by crystallization from solution or by direct synthesis from the elements, that is by solid-state reactions. (We exclude gaseous clusters here since they are not structurally well characterized.) Members of the first group belong to the well known class of Zintl ions and include anions of group 14 (the tetrels (Tt):  $\text{Tt}_6^{4-}$ ,

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$\text{Tt}_9^{3-}$ ,  $\text{Tt}_5^{2-}$ ,  $\text{Tt}_9^{2-}$ , and  $\text{Tt}_{10}^{2-}$ ), of group 15 (the pnictogens (Pn):  $\text{Pn}_4^{2-}$ ), and the mixed species  $\text{Tt}_2\text{Pn}_2^{2-}$ ,  $\text{Tr}\text{Tt}_8^{3-}$ , and  $\text{Tr}\text{Tt}_9^{3-}$  ( $\text{Tr}$  = element of group 13).<sup>[1-3]</sup> These clusters form when the corresponding alloy with Na or K (or mixtures of them) is dissolved in either liquid ammonia or ethylenediamine, often mixed with 2,2,2-crypt.<sup>[4]</sup> Most of these clusters have been characterized in terms of nuclearity and charge by NMR spectroscopy in solution.<sup>[5]</sup> Presumably, formation of the cluster takes place during the extraction with the solvent since no such clusters have been observed in the starting alloys.<sup>[2,6]</sup> The group of clusters made by solid-state reactions is somewhat more diverse in terms of sizes and charges, and comprises primarily clusters of group 13 (the triels (Tr):  $\text{Tr}_{11}^{7-}$ ,  $\text{Tr}_{12}^{8-}$ ,  $\text{Tr}_5^{7-}$ ,  $\text{Tr}_5^{9-}$ ,  $\text{Tr}_6^{8-}$ ,  $\text{Tr}_6^{6-}$ ,  $\text{Tr}_6^{6-}$ ,  $\text{Tr}_{12}(\text{Tr})^{11-}$ ,  $\text{Tr}_{12}(\text{Zn}, \text{Cd} \text{ or } \text{Hg})^{12-}$ ,  $\text{Tr}_{10}(\text{Zn})^{8-}$ , and  $\text{Tr}_{10}(\text{Ni}, \text{Pd} \text{ or } \text{Pt})^{10-}$ ), but also includes a few species from groups 14 ( $\text{Tt}_4^{4-}$ ), 15 ( $\text{Bi}_8^{2+}$ ,  $\text{Bi}_5^{3+}$ ,  $\text{Bi}_5^{5+}$ ), and 16 ( $\text{Se}_4^{2+}$  and  $\text{Te}_4^{2+}$ ).<sup>[2]</sup> These clusters are found in solid-state compounds with alkali metals as counterions (or  $\text{AlCl}_4^-$  as counteranions), and are made by direct synthesis from the corresponding elements. Despite this big variety of deltahedral clusters in the two groups none has been made both by synthesis from solution and by solid-state reaction.

In  $\text{Ge}_9^{4-}$  we have found the first such species to bridge the two classes. Prior to this report the clusters of  $\text{Ge}_9^{4-}$  were structurally characterized only in the salt  $[\text{K}^+ \cdot 222\text{-crypt}]_6(\text{Ge}_9^{4-})(\text{Ge}_9^{4-})$ , made by crystallization of a solution of a K-Ge alloy dissolved in ethylenediamine.<sup>[7]</sup> The tin-substituted isoelectronic clusters  $[\text{Ge}_{9-x}\text{Sn}_x]^{4-}$  ( $x = 1-8$ ) have been characterized in solution by  $^{119}\text{Sn}$  NMR spectroscopy.<sup>[5]</sup> Transition metal derivatives of these and similar deltahedral Zintl ions are also known. They include  $[\text{Tt}_9\text{Cr}(\text{CO})_3]^{4-}$  ( $\text{Tt} = \text{Sn}, \text{Pb}$ ),  $[\text{Sn}_6\{\text{Cr}(\text{CO})_5\}_6]^{2-}$ , and the recently synthesized Ge-centered  $[\text{Ge}_9\text{Ni}(\text{PPh}_3)]^{2-}$ , all of which have been isolated with cryptated alkali metal cations and structurally characterized.<sup>[8]</sup> Similarly  $[\text{Tt}_9\text{PtL}_x]^{4-}$  ( $\text{Tt} = \text{Sn}, \text{Pb}$ ; L = ligand) have been characterized in solution by  $^{119}\text{Sn}$  and  $^{207}\text{Pb}$  NMR spectroscopy.<sup>[9]</sup>

We have now made the naked  $\text{Ge}_9^{4-}$  clusters in "neat" solids.<sup>[10]</sup> These solids are  $\text{Cs}_4\text{Ge}_9$  and the isostructural  $\text{Rb}_4\text{Ge}_9$ , both made by direct synthesis from the corresponding elements (see *Experimental Section*).  $\text{Ge}_9^{4-}$  is the first deltahedral cluster of the tetrads in the solid state since  $\text{Tt}_4^{4-}$  was made more than forty years ago in  $\text{A}_4\text{Tt}_4$  ( $\text{A}$  = alkali metal).<sup>[11]</sup> Our attempts to make similar  $\text{A}_4\text{Ge}_9$  compounds with sodium or potassium proved unsuccessful. This supports the hypothesis that the precursor alloys used for the solution studies (traditionally made with the light alkali metals) do not contain the clusters.

The structure of  $\text{Cs}_4\text{Ge}_9$  (Figure 1) was determined by single-crystal X-ray diffraction (see *Experimental Section*). It crystallizes in the rare noncentrosymmetric  $P4_1$  space group and contains four crystallographically different but

otherwise very similar  $\text{Ge}_9$  clusters A, B, C, and D. The structure can be viewed as containing quite open layers made of clusters A, B, and C, and positioned perpendicular to the  $c$  axis at  $z \approx 1/12, 4/12, 7/12$ , and  $10/12$ . These layers alternate with clusters D centered along the  $4_1$  screw axis (the axis is at  $1/2, 1/2, z$ ) at  $z \approx 5/24, 11/24, 17/24$ , and  $23/24$ . The clusters are well separated from each other by the large cesium cations positioned within and between the layers. These cations cap triangular and square faces of the clusters and also bridge some edges and "cap" some vertices. The shortest intercluster distance is  $3.956(8)$  Å.

All four clusters are monocapped square antiprisms with very similar dimensions (Figure 2 and Table 1). The stoichiometry of the compounds combined with the observation that they are also electronically balanced (below), that is Zintl phases, defines the charge of each cluster as  $4^-$ . This is also consistent with Wade's rules which predict a charge of  $4^-$  for such *nido* species.<sup>[12]</sup> Furthermore, extended Hückel molecular orbital calculations show very similar HOMO-LUMO gaps for the four clusters at 40 electrons (2.88, 2.91, 2.91, and 3.18 eV), that is at a charge of  $4^-$ .

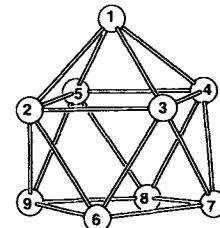


Figure 2. View of one of the four crystallographically different  $\text{Ge}_9^{4-}$  clusters (cluster A). All four clusters have the same geometry of a monocapped square antiprism. The numbering system serves for the assignment of the atoms in Table 1.

Table 1. Important Ge-Ge intracluster distances for the four different clusters in  $\text{Cs}_4\text{Ge}_9$  (at 173 K) and for  $\text{Ge}_9^{4-}$  in  $[\text{K}^+ \cdot 222\text{-crypt}]_6(\text{Ge}_9^{4-})(\text{Ge}_9^{4-})$  [7]. The numbering of the atoms is given in Figure 2.

Atom 1 - Atom 2	Cluster A	Cluster B	Cluster C	Cluster D	$\text{Ge}_9^{4-}$ from [7]
Ge1-Ge2	2.566(8)	2.522(8)	2.553(9)	2.585(8)	2.544(6)
Ge3	2.560(9)	2.556(8)	2.563(9)	2.591(8)	2.560(6)
Ge4	2.582(9)	2.591(9)	2.575(9)	2.575(8)	2.569(7)
Ge5	2.609(9)	2.588(9)	2.565(8)	2.577(8)	2.578(6)
Ge2-Ge3	2.876(8)	2.997(8)	3.008(11)	2.991(8)	2.962(7)
Ge5	2.777(8)	2.817(8)	2.744(9)	2.701(8)	2.703(6)
Ge6	2.556(8)	2.560(8)	2.560(9)	2.579(9)	2.585(6)
Ge9	2.604(8)	2.590(8)	2.590(9)	2.568(8)	2.538(7)
Ge3-Ge4	2.823(9)	2.770(8)	2.717(9)	2.763(8)	2.764(6)
Ge6	2.550(8)	2.584(9)	2.544(10)	2.601(9)	2.583(5)
Ge7	2.568(9)	2.586(8)	2.561(10)	2.584(9)	2.561(6)
Ge4-Ge5	2.825(9)	2.808(8)	2.866(9)	2.803(8)	2.799(6)
Ge7	2.609(9)	2.658(8)	2.637(9)	2.592(8)	2.646(6)
Ge8	2.597(9)	2.593(9)	2.581(9)	2.588(8)	2.590(5)
Ge5-Ge8	2.593(9)	2.582(9)	2.534(9)	2.590(8)	2.601(6)
Ge9	2.638(8)	2.638(8)	2.630(8)	2.631(8)	2.659(5)
Ge6-Ge7	2.609(9)	2.596(8)	2.544(10)	2.619(9)	2.561(7)
Ge9	2.618(8)	2.591(8)	2.574(9)	2.588(8)	2.557(6)
Ge7-Ge8	2.579(9)	2.591(9)	2.611(10)	2.589(8)	2.562(7)
Ge8-Ge9	2.600(8)	2.550(8)	2.571(9)	2.605(8)	2.533(7)
Ge6-Ge8	3.730(8)	3.715(8)	3.841(10)	3.802(8)	3.638(7)
Ge7-Ge9	3.624(8)	3.581(8)	3.410(10)	3.543(8)	3.580(7)

The geometry of the four clusters is virtually the same as that of the Ge clusters in the K-crypt salt.<sup>[7]</sup> The distances of the latter are listed in Table 1 for comparison. Often it is difficult to distinguish between a nine-atom *closo* species (a tricapped trigonal prism) and a nine-atom *nido* species (a monocapped square antiprism). However, the four clusters in the present compound are unambiguously *nido* polyhedra according to their distances. The diagonals of the square bases, Ge6-Ge8 and Ge7-Ge9 (Table 1), which are the potential candidates for heights in even-

Figure 1. A general view of the tetragonal unit cell of  $\text{Cs}_4\text{Ge}_9$  (the  $c$  axis runs vertical). Bonds are drawn between the Ge atoms of the four different  $\text{Ge}_9^{4-}$  clusters. The Cs atoms are shown isolated. All atoms are drawn with 50% thermal ellipsoids.

tual trigonal prisms, are quite longer than the “existing” heights, Ge<sub>3</sub>–Ge<sub>4</sub>, Ge<sub>2</sub>–Ge<sub>5</sub> and Ge<sub>2</sub>–Ge<sub>3</sub>, Ge<sub>4</sub>–Ge<sub>5</sub>, respectively. The similarities in shape and distances between the four clusters in Cs<sub>4</sub>Ge<sub>9</sub> and the one in [K<sup>+</sup>-222-crypt]<sub>6</sub>(Ge<sub>9</sub>)-(Ge<sub>9</sub>) support the assumption that the latter is indeed Ge<sub>9</sub><sup>4-</sup>. This is contrary to a recent suggestion that the two clusters in the crypt-salt are both Ge<sub>9</sub><sup>3-</sup> similar to the recently discovered Sn<sub>9</sub><sup>3-</sup> and Pb<sub>9</sub><sup>3-</sup> in [K<sup>+</sup>-222-crypt]<sub>6</sub>(Sn<sub>9</sub><sup>3-</sup>)(Sn<sub>9</sub><sup>3-</sup>) and [K<sup>+</sup>-222-crypt]<sub>6</sub>(Pb<sub>9</sub><sup>3-</sup>)(Pb<sub>9</sub><sup>3-</sup>), respectively, as well as to Ge<sub>9</sub><sup>3-</sup> in [K<sup>+</sup>-222-crypt]<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>(Ge<sub>9</sub><sup>3-</sup>) and [K<sup>+</sup>-222-crypt]<sub>3</sub>(Ge<sub>9</sub><sup>3-</sup>).<sup>[13]</sup>

The Cs<sub>4</sub>Ge<sub>9</sub> compound is a semiconductor (or an insulator) according to its magnetic susceptibility (temperature independent and near zero, see *Experimental Section*) and its appearance (semitransparent, ruby-red color).

The Cs–Ge and Rb–Ge phase diagrams are quite uncertain especially in the regions with high alkali metal content.<sup>[14]</sup> There are conflicting reports on the number of Cs–Ge and Rb–Ge compounds. Three possible stoichiometries, A<sub>3</sub>Ge, A<sub>3</sub>Ge<sub>2</sub>, and AGe<sub>4</sub> (A = Rb or Cs), are suggested in each phase diagram, but only CsGe and RbGe have been structurally characterized. The compounds with the stoichiometries closest to A<sub>4</sub>Ge<sub>9</sub> (30.8 at. % alkali-metal) would be AGe<sub>4</sub> (20 at % alkali metal), which melt congruently at 990 °C and 1110 °C for Cs and Rb, respectively.

The absence of large naked clusters of group 14 in the solid state may be explained by the large ratio of nuclearity to charge. According to Wade’s rules deltahedral clusters of this group will have charges of 2-, 4-, and 6- for *clos*, *nido*, and *arachno* species, respectively. It is important to note that these charges are independent of the nuclearity of the cluster. The charge balancing cations therefore may not be enough to efficiently keep apart (shield) large clusters. This is especially true for the smaller alkali metals such as Na and K which have been traditionally used as counterions. The effect is even more pronounced when the corresponding tetrel is among the heaviest of the group (Sn or Pb), which results in even larger clusters. In the crypt salts the large alkali metal cryptate is sufficient to separate the clusters efficiently. The new compounds are most likely the result of the combination of large cations (cesium or rubidium) and clusters of the small germanium. Despite the relatively high nuclearity and the relatively small negative charge of 4-, the clusters are small enough that four large cations can separate them efficiently.

### Experimental Section

**Synthesis:** Ruby-red semitransparent Cs<sub>4</sub>Ge<sub>9</sub> was initially isolated and its structure determined from a reaction of Cs, Na, Al, and Ge loaded in atomic ratio of 4:1:1:10. The mixture was heated at 800 °C for five days in sealed Nb containers closed in evacuated quartz ampoules. The furnace was slowly cooled to room temperature at a rate of 5 °C per hour. After the stoichiometry of the compound was determined from the single crystal work, a single-phase product of Cs<sub>4</sub>Ge<sub>9</sub> ( $\geq 97\%$  according to a Guinier powder pattern) was synthesized by heating a stoichiometric mixture of the elements (in Ta containers) at 800 °C for 1 h, quenching it in cold water, and then annealing it at 300 °C for 12 days. Rb<sub>4</sub>Ge<sub>9</sub> (ruby-red, semitransparent,  $a = 15.154(8)$  and  $c = 30.82(4)$  Å from 13 measured lines, extremely weakly diffracting) was made similarly.

**Structure determination:** Data were collected from a single crystal (0.15 × 0.08 × 0.08 mm) on a Siemens SMART system with monochromated Mo<sub>Kα</sub> radiation at 173 K ( $2\theta_{\max} = 45^\circ$ ), and corrected for absorption by semiempirical methods. The structure was solved by direct methods. Full-matrix least-squares refinement on  $F^2$  of all atoms with anisotropic thermal parameters using SHELXTL V5.0 converged with  $R1 = 0.064$  for 5128 independent reflections with  $I > 3\sigma_i$  ( $R1/wR2 = 0.093/0.189$  for 6475 independent reflections with  $I > 2\sigma_i$ ) and 469 parameters. Crystal data: Cs<sub>4</sub>Ge<sub>9</sub>, tetragonal,  $P4_1$ , with  $a = 15.5074(5)$ ,  $b = 31.3997(9)$  Å,  $V = 7551.0(6)$  Å<sup>3</sup>,  $Z = 16$ ,  $\rho_{\text{calcd}} = 4.17$  g cm<sup>-3</sup>,  $\mu = 215.73$  cm<sup>-1</sup>. The compound diffracts very poorly. Data sets collected on the Siemens diffractometer from three different crystals showed very low ratios of observed to measured reflections. Further details of the crystal structure investigation may be obtained from the Fachin-

formationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-406486.

**Magnetic measurements:** The magnetization of 25 mg of the Cs<sub>4</sub>Ge<sub>9</sub> sample, which was obtained in near 100% yield, was measured at field of 3 T over the range of 6–295 K (Quantum Design MPMS SQUID magnetometer). The raw data, corrected for the susceptibility of the holder and the ion-core dimagnetism arising from four Cs<sup>+</sup> and nine Ge<sup>4+</sup> ions, lay between  $-3.79$  and  $-3.47 \times 10^{-4}$  emu mol<sup>-1</sup>. Correction for diamagnetism due to the Larmor precession of the delocalized lone pairs of electrons on cluster orbitals ( $-3.0 \times 10^{-4}$  emu mol<sup>-1</sup>) was also applied.<sup>[15]</sup> The corrected molar susceptibility is virtually zero, and fluctuates between  $-7.9 \times 10^{-5}$  and  $4.6 \times 10^{-5}$  emu mol<sup>-1</sup>.

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- [1] The use of triels, tetrels, and pentels or pnictogens has been suggested by the Commission of Nomenclature of Inorganic Chemistry in the Inorganic Chemistry Division of IUPAC; B. P. Block, W. H. Powell, W. C. Fernelius *Inorganic Chemical Nomenclature: Principles and Practice*, American Chemical Society, Washington, DC, 1990, p. 24.
- [2] J. D. Corbett, *Struct. Bonding*, (Berlin) 1997, 87, 157, and references therein.
- [3] J. D. Corbett, *Chem. Rev.* 1985, 85, 383, and references therein.
- [4] 2,2,2-crypt is an abbreviation for 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane.
- [5] W. L. Wilson, R. W. Rudolph, L. L. Lohr, R. C. Taylor, P. Pykkö, *Inorg. Chem.* 1986, 25, 1535, and references therein.
- [6] To the best of our knowledge there are no systematic studies on the precursor alloys. Kummer and Diehl (D. Kummer, L. Diehl, *Angew. Chem.* 1970, 82, 881; *Angew. Chem. Int. Ed. Engl.* 1970, 9, 895) report mixture of unidentified phases and metallic tin in a Na–Sn precursor.
- [7] C. H. E. Belin, J. D. Corbett, A. Cisar, *J. Am. Chem. Soc.* 1977, 99, 7163.
- [8] B. W. Eichhorn, R. C. Haushalter, W. T. Pennington, *J. Am. Chem. Soc.* 1988, 110, 8704; B. W. Eichhorn, R. C. Haushalter, *J. Chem. Soc. Chem. Commun.* 1990, 937; B. Schiemenz, G. Huttner, *Angew. Chem.* 1993, 105, 295; *Angew. Chem. Int. Ed. Engl.* 1993, 32, 297; D. R. Gardner, J. C. Fettinger, B. W. Eichhorn, *ibid.* 1996, 108, 3032; *Angew. Chem. Int. Ed. Engl.* 1996, 35, 2852.
- [9] F. Teixidor, M. L. Luetkens, Jr., R. W. Rudolph, *J. Am. Chem. Soc.* 1983, 105, 149.
- [10] The use of “neat” here (after J. D. Corbett in ref. [2]) is to distinguish solids made by solid-state reactions from “molecular” solids crystallized from solution.
- [11] R. E. Marsh, D. P. Shoemaker, *Acta Crystallogr.* 1953, 6, 197; On page 265 of the textbook *Advanced Inorganic Chemistry* (F. A. Cotton, G. Wilkinson, Wiley, New York, 5th ed., 1988) it is erroneously implied that Na<sub>4</sub>Pb<sub>9</sub> and Na<sub>4</sub>Sn<sub>5</sub> are known and structurally characterized. The only known Pb<sub>9</sub><sup>4+</sup> and Sn<sub>5</sub><sup>3-</sup> ions are found in [K<sup>+</sup>-222-crypt]<sub>3</sub>KPb<sub>9</sub> (J. Cambell, D. A. Dixon, H. P. Mercier, G. J. Schrobilgen, *Inorg. Chem.* 1995, 34, 5798) and [Na<sup>+</sup>-222-crypt]<sub>2</sub>Sn<sub>5</sub> (P. A. Edwards, J. D. Corbett, *Inorg. Chem.* 1977, 16, 903), respectively.
- [12] K. Wade, *Adv. Inorg. Chem. Radiochem.* 1976, 18, 1.
- [13] T. F. Fässler, M. Hunziker, *Z. Anorg. Allg. Chem.* 1996, 622, 837; V. Angilella, C. Belin, *J. Chem. Soc. Faraday Trans.* 1991, 87, 203; C. Belin, H. Mercier, V. Angilella, *New J. Chem.* 1991, 15, 931; T. F. Fässler, M. Hunziker, *Inorg. Chem.* 1994, 33, 5380.
- [14] M. E. Drits, V. F. Potemkin, L. L. Zusman, *Inorg. Mater.* 1982, 18, 969; A. N. Orlov, K. A. Chuntonov, L. Z. Melkhov, A. A. Semyannikov, *Russ. Metall.* 1987, 6, 176; In *Binary Alloy Phase Diagrams* (Ed: T. B. Massalski), ASM International, Materials Park, Ohio, 1990) the area of uncertainty is erroneously shown at the Ge-rich side rather than the Cs-rich side.
- [15] N. W. Ashcroft, D. N. Mermin, *Solid State Physics*, Holt, Reinhart and Wilson, Philadelphia, 1976, p. 649.