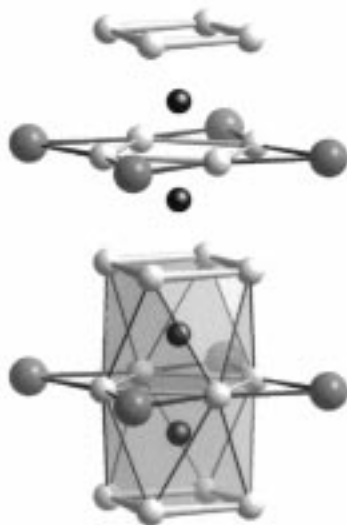
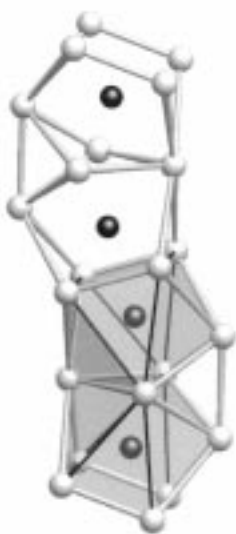
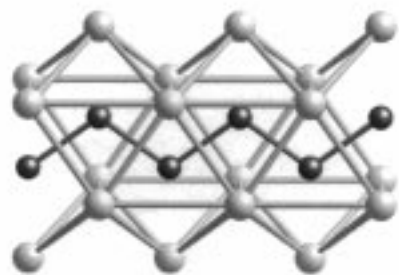


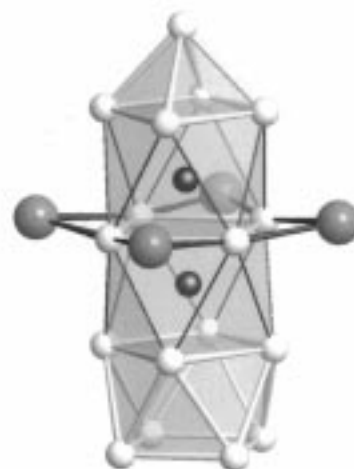
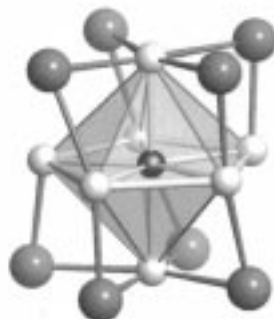
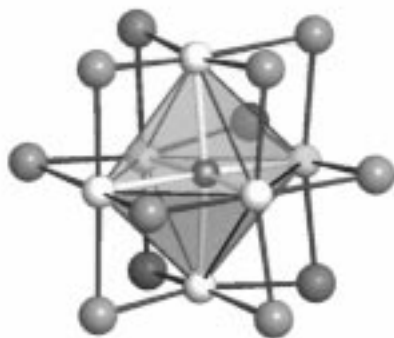
## Low-Dimensional Metals



## Subhalides



## Bismuth Polycations



## Cluster Compounds

# From the Metal to the Molecule—Ternary Bismuth Subhalides

Michael Ruck\*

Subvalent compounds, that is, metal-rich substances in which the average oxidation state of the cation is smaller than would be expected from the  $(8 - N)$  rule, have proved to be a rich source of unexpected structural and physical features. The extraordinary structural chemistry generally observed in subvalent compounds is a consequence of the low and often non-integer oxidation states of the metal atoms coupled with the low concentration of valence electrons. Both factors can lead to a wide-range of bonding types within the same compound. A characteristic of

these compounds is the interplay between “metallic” regions, with delocalized electrons and mainly nonpolar bonds between the metal atoms, and “saltlike” regions, which are characterized by strong localization of the electrons and heteropolar exchange between the metal and nonmetal atoms. The volumes of the different structural regions as well as the extent to which they interpenetrate can vary from compound to compound. The ternary subhalides of bismuth belong to a new class of substances which cover the whole spectrum from parti-

ally oxidized “porous” metals, through one- and two-dimensional metals, up to semiconducting ionic or molecular cluster compounds. These subvalent compounds with their unusually high chemical stabilities provide excellent vehicles for further research and their potential is described in the following article.

**Keywords:** bismuth • cluster compounds • intermetallic phases • low-dimensional metals • subvalent compounds

## 1. Introduction

In spite of the difficulties, there is a certain satisfaction in establishing the rules and limitations of using localized bonding concepts to understand the binding in a large collection of atoms in the metallic state. Since practically all the typical physical properties of a metal depend on the almost free movement of electrons in the solid, the question arises: what happens when the freedom of movement of the conduction electrons is reduced by chemical means? Restricting the mobility of electrons to one dimension can affect quantum mechanical behavior and, as a result, macroscopic effects, which can be expected to be different from those of conventional three-dimensional metals. Further limitation must lead at some point to the crossing of the boundary between metallic and semiconducting behavior.

Solid-state chemistry can contribute to the investigation of this boundary area through the synthesis and characterization

of a range of chemically similar substances that demonstrate well-defined tiny steps in the transition between three-dimensional metallic and semiconducting materials. In a chemical sense, this typically involves metal-rich subvalent compounds. Famous examples are the suboxides and subnitrides of alkali and alkaline earth metals. Their structures can be roughly described as a metallic matrix in which ionic islands or rods are embedded.<sup>[1]</sup> The saltlike building blocks mostly consist of oxygen or nitrogen-centered  $[MX_6]$  octahedra that are either isolated or linked together by faces to form oligomeric or polymeric units. Less commonly observed are highly complex building blocks like, for example, the  $[Ba_{14}CaN_6]$  cluster in  $Na_{14}Ba_{14}CaN_6$ <sup>[2]</sup> or the  $[O_7(Al_2Ba_{17})]$  cluster in  $Ba_{17}Al_3O_7$ .<sup>[3]</sup> The latter subvalent metallate is also distinctive in that the Al atoms coexist as cationic and metallic species. In addition, the ternary and quaternary compounds provide a link to intermetallic phases, the structural motifs of which are also observed in the metallic matrices of subvalent compounds.

The metal-rich halides and chalcogenides of electron-deficient transition elements probably form the most extensive group of subvalent compounds.<sup>[4]</sup> Structural investigations reveal that a large range of cluster types occur for these compounds although the  $M_6X_8$  and  $M_6X_{12}$  types are dominant. Often these clusters are stabilized by interstitial atoms (e.g. H, B, C, N, platinum metals). Increasing the ratio of metal to

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nonmetal atoms leads, by progressive condensation of the clusters, to increasingly extended metallic regions.<sup>[5]</sup>

Such subvalent compounds are not only known for electron-deficient s-, d-, and f-metals, but also for p-(semi-)metals albeit with far fewer examples. For example, recently significant progress has been made especially in research using the elements indium,<sup>[6]</sup> tin,<sup>[7]</sup> and bismuth.<sup>[8]</sup> This research mainly concerns the ternary and quaternary oxides or halides of the aforementioned main group elements which contain electron-rich transition metals from Groups 8–10 as further components. Among these compounds, of particular note are the subhalides of bismuth, which show a large variation in metal/nonmetal ratios and range from partially oxidized intermetallic phases to complex salts and molecular solids. Consequently, there is a remarkable wealth of structural motifs that are not simply different arrangements of identical building blocks, but generally represent unique structures for each system.

The crystal structures of the binary bismuth halides already give a first impression of the structural variability, which is fully developed in the ternary phases. The bismuth monohalides  $\text{BiBr}^{[9]}$  and  $\text{BiI}^{[10]}$  like the metal-rich compounds  $\text{Bi}_{14}\text{I}_4^{[11]}$  and  $\text{Bi}_{18}\text{I}_4^{[12]}$  consist of one-dimensional (1D) infinite strips (Figure 1). The arrangement of the Bi atoms is similar to that in elemental bismuth, so that the overall impression is that the halogen atoms have acted as “chemical scissors” by cutting out strips from the element structure. Independent of this 1D character of the structural building blocks is that the electrons are mainly localized so that  $\text{BiBr}$ , which can be formulated as  $(\text{Bi}^0)(\text{Bi}^{\text{II}})\text{Br}_{4/2}$ , acts as a semiconductor.

Although their chemical composition differs only slightly from that of the monohalides the slightly halogen-rich compounds  $\text{Bi}_6\text{Cl}_7^{[13]}$  and  $\text{Bi}_6\text{Br}_7^{[9]}$  possess a completely different architecture: they contain polyhedral  $\text{Bi}_9^{5+}$  polycations (Figure 2), which are embedded in a coordination environment of halogenobismuthate(III) anions. Pictorially this can be regarded as a saltlike matrix in which “metallic” islands (more correctly, islands with metal–metal bonds) are scattered. It is possible to crystallize the  $\text{Bi}_9^{5+}$  polycations with complex counter ions as seen in compounds of the type  $\text{Bi}_{10}\text{M}_3\text{X}_{18}$  ( $\text{M} = \text{Zr}, \text{Hf}; \text{X} = \text{Cl}, \text{Br}$ ).<sup>[14]</sup> Similarly, tetrachlorometallate(III) anions stabilize the antiprismatic  $\text{Bi}_8^{2+}$  ion in  $\text{Bi}_8(\text{AlCl}_4)_2^{[15]}$  as well as the trigonal bipyramidal  $\text{Bi}_5^{3+}$  ion in  $\text{Bi}_5(\text{AlCl}_4)_3^{[16]}$  and  $\text{Bi}_5(\text{GaCl}_4)_3^{[17]}$

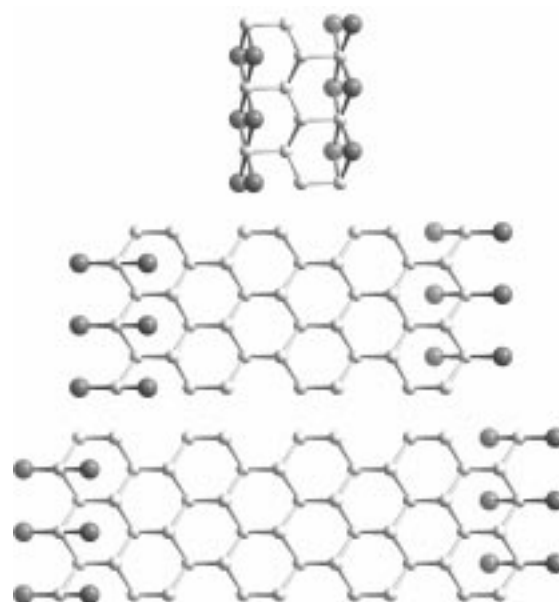


Figure 1. One-dimensional strings in the structures of  $\text{BiI}$  ( $=\text{Bi}_4\text{I}_4$ ),  $\text{Bi}_{14}\text{I}_4$ , and  $\text{Bi}_{18}\text{I}_4$ . The Bi atoms are shown lightly shaded.

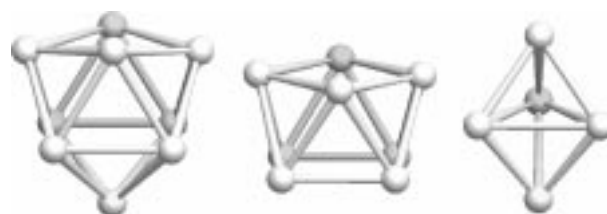


Figure 2. Homonuclear bismuth polycations in binary subhalides and halogenometallates:  $\text{Bi}_9^{5+}$ ,  $\text{Bi}_8^{2+}$ , and  $\text{Bi}_5^{3+}$

In the case of the new ternary bismuth subhalides, which will be described and discussed subsequently, we are concerned with subhalides of intermetallic phases rather than halogenometallates of the type mentioned above. The extent of the metallic areas for each structure serves as a means of categorizing the compounds. Starting with three-dimensional metals, the structures of which are disrupted by pores that are filled with anions, a reduction in the dimensionality of the metallic system ensues until finally, isolated clusters of metal atoms result. Firstly, a brief description of the synthesis of such compounds is given.



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## 2. The Partial Oxidation of Intermetallic Phases

In principle, the synthesis of the subhalides should proceed by heating the elements in an evacuated quartz ampoule. Mostly, it is found to be more convenient to use intermetallic phases or metal halides as starting materials. In some cases, it is necessary to add auxiliary reagents, such as niobium halides, which modify the partial pressures in the gas phase through various equilibrium processes but are not incorporated into the bismuth subhalides and can be easily separated after the reaction is complete. That electron-rich transition metals of Groups 8–10 are particularly suitable for the formation of ternary bismuth subhalides is because of a number of favorable factors:

- 1) With the exception of cobalt, these elements form intermetallic phases with bismuth. Previous studies suggest that this is a basic requirement for the formation of the corresponding subhalides. Consequently, we can speak of the partial oxidation of intermetallic phases.
- 2) The electronegativities of these transition metal elements hardly differ from that of bismuth so that the formation of strongly heteropolar bismuthides is unlikely.
- 3) Bromine and iodine oxidize these transition elements to di- or trihalides, high oxidation states, which make the formation of the subhalides improbable, are avoided.
- 4) The halides of these transition metals are volatile at temperatures at which bismuth and bismuth halides exist in the gas phase. This gives a route for the separation of the products from the gas phase.

Although many subhalides can be crystallized directly from the melt, in some cases the option of gas-phase transport can be used. The principle of subjecting two metals to a simultaneous chemical transport to deposit them as an intermetallic phase is well known, but has only recently been more thoroughly investigated.<sup>[18]</sup> That subvalent compounds can also be deposited has been shown for the first time with the coupled transport of palladium and aluminum with iodide, whereby in addition to a variety of intermetallic phases the ternary subiodide  $\text{Pd}_5\text{AlI}_2$  was formed.<sup>[19]</sup>

For many reasons, it is difficult to synthesize pure bismuth subhalides, most of the compounds decompose and form peritectically. Frequently, the liquid phase separates below a critical temperature into a halogen-rich and an extremely halogen-deficient melt. In addition, at reaction temperatures which are usually over 400 °C there are significant amounts of bismuth vapor and gas-phase bismuth halides, which precipitate out on cooling. Discovering suitable reaction conditions is made difficult by the often fragmentary nature of the phase diagrams. The calculation of transport equilibria also fails because of the paucity of thermodynamic data and insufficient knowledge regarding the gas-phase species. The possibility of observing new ternary bismuth subhalides in the ternary systems, where new compounds have already been discovered, as well as those, which up to now have looked less promising, cannot be ruled out.

The chemical properties of the binary and ternary subhalides of bismuth are particularly noteworthy. Remarkably, the compounds are only slightly sensitive to oxidation. In this way, they differ significantly from most other subvalent

compounds. All bismuth halides can be left exposed to the air for several days to several months without appreciable decomposition and some are even resistant to attack from dilute mineral acids.

## 3. “Porous” Metals

Bismuth forms two intermetallic phases with nickel, these are  $\text{BiNi}$  and  $\text{Bi}_3\text{Ni}$ , which decompose peritectically at 655 °C and 469 °C, respectively.<sup>[20]</sup> If both elements are treated with iodine at temperatures higher than the decomposition temperature of  $\text{Bi}_3\text{Ni}$ , the subiodide  $\text{Bi}_{5.6}\text{Ni}_5\text{I}$  is obtained by gas-phase transport.<sup>[21]</sup>

That the crystals form as needles suggests a marked anisotropy of the crystal structure. The latter mostly consists of double-walled decagonal-cross-section tubes made up of Ni and Bi atoms (Figure 3). In each tube, the metal atoms are

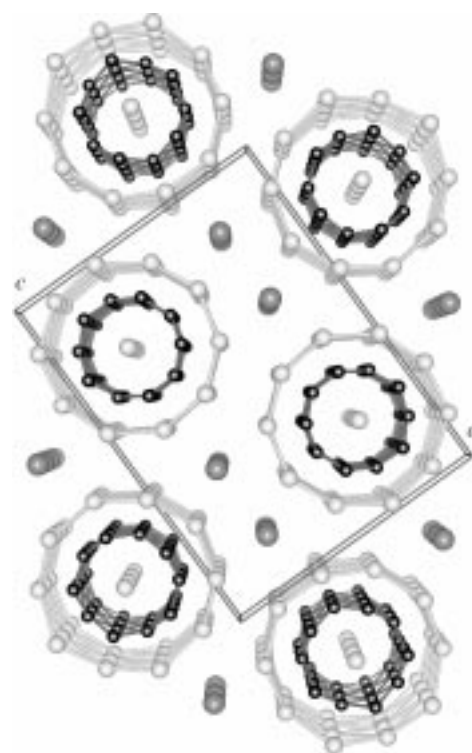


Figure 3. The crystal structure of  $\text{Bi}_{5.6}\text{Ni}_5\text{I}$ . Connecting lines highlight the intermetallic structural part formed by decagonal-cross-sectioned channels of Bi and Ni atoms. Ni atoms are shown in black.

arranged in regular pentagons, which are stacked in staggered conformations. On the central axis of the concentric tubes, there are additional Bi atoms so that compact metallic rods with a diameter of more than 1.1 nm result. Because of the noncrystallographic imposed symmetry of the rods, corresponding to a fivefold rotoinversion axis, close-packing of the rods is impossible. The remaining “pores” contain the iodide ions, which, however cannot be removed from the structure without decomposition of the subiodide.

$\text{Bi}_{5.6}\text{Ni}_5\text{I}$  is a moderately good conductor, and its resistance increases with temperature (Figure 4). The conduction of

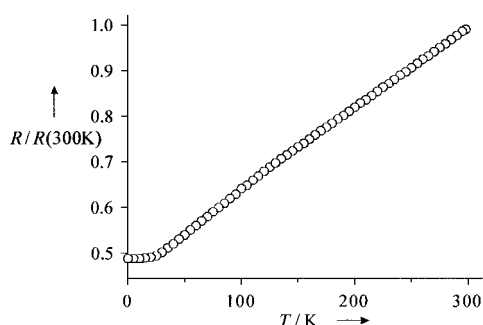


Figure 4. Temperature dependence of the electrical resistance of a crystal of  $\text{Bi}_{5.6}\text{Ni}_5\text{I}$  measured parallel to the intermetallic rods of the structure.

the electrons takes place mostly in the interior of the individual intermetallic rods, since the double rows of the iodide ions are areas of electron localization and the metallic rods have only small contact areas. One could visualize a needle-crystal of  $\text{Bi}_{5.6}\text{Ni}_5\text{I}$  as a bundle of parallel, partially isolated, metallic fibers.

$\text{Bi}_{12}\text{Rh}_3\text{Br}_2$ , another “porous” metal, is built-up in a completely different way.<sup>[22]</sup> The crystal structure is based on an open three-dimensional framework of rhodium-centered  $[\text{RhBi}_{8/2}]$  cubes and square antiprisms, which share common edges (Figure 5). Bromide ions fill the chiral pores of the

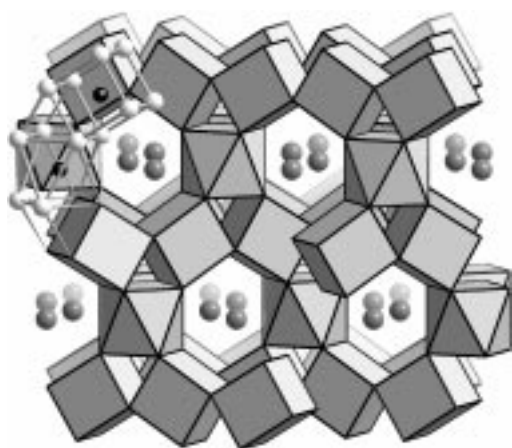


Figure 5. Section of the structure of  $\text{Bi}_{12}\text{Rh}_3\text{Br}_2$ . Edge-sharing  $[\text{RhBi}_{8/2}]$  cubes and square  $[\text{RhBi}_{8/2}]$  antiprisms form a network of chiral channels in which bromide ions are embedded.

intermetallic framework. Writing the sum formula of  $\text{Bi}_{12}\text{Rh}_3\text{Br}_2$  as  $(\text{Bi}_4\text{Rh})_3\text{Br}_2$  emphasizes the close correspondence to the intermetallic phase  $\alpha\text{-Bi}_4\text{Rh}$ . Similar to the subbromide, the cubic crystal structure of  $\alpha\text{-Bi}_4\text{Rh}$  consists of edge-sharing  $[\text{RhBi}_{8/2}]$  polyhedra.<sup>[23]</sup> By calculating the electron localization function (ELF) for  $\alpha\text{-Bi}_4\text{Rh}$  it was recently shown that the lone pairs of the Bi atoms are located at the surface of the polyhedra, pointing away from the metallic bonding inside the framework.<sup>[24]</sup> This concept can be transferred to the partly oxidized subbromide  $\text{Bi}_{12}\text{Rh}_3\text{Br}_2$ , too. Thus, there is a comparable structural segregation of regions with largely delocalized electrons (conduction electrons inside the framework of  $[\text{RhBi}_{8/2}]$  polyhedra) and areas with

high electronic localization (lone pairs on the framework surface and bromide ions in the pores).

#### 4. Two-Dimensional Metals

Similar to  $\text{Bi}_{12}\text{Rh}_3\text{Br}_2$ , the intermetallic part of the structure of  $\text{Bi}_{13}\text{Pt}_3\text{I}_7$  consists of edge-sharing  $[\text{PtBi}_{8/2}]$  cubes (Figure 6).<sup>[25]</sup> In this case, the linking of the polyhedra only occurs in two dimensions resulting in a planar net of the Kagomé type. The hexagonal prismatic voids in the net each provide space for an iodide ion. The layers in the structure are separated from each other by alternating layers of iodide ions and sheets made up of parallel  $\infty[\text{BiI}_4^-]$  zigzag chains.

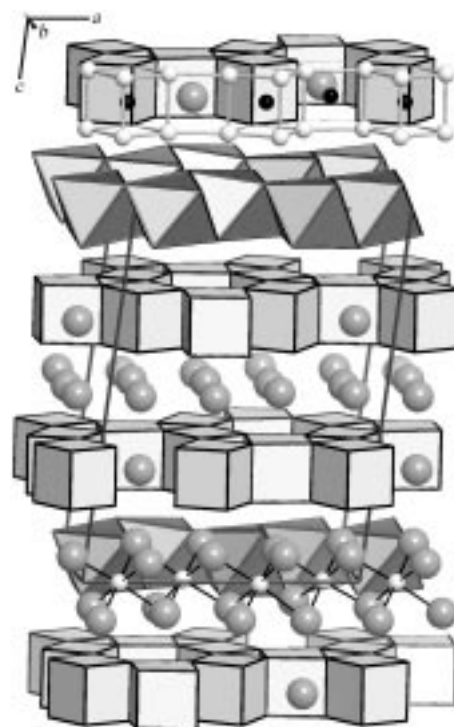


Figure 6. The crystal structure of  $\text{Bi}_{13}\text{Pt}_3\text{I}_7$ . The edge-sharing  $[\text{PtBi}_{8/2}]$  cubes form a Kagomé net in which iodide ions fill the hexagonal prismatic holes. Monolayers of individual iodide ions and layers of tetraiodobismuthate(III) chains lie between the nets.

The cubic coordination of the Pt atoms is interesting since in the binary intermetallic phases the Pt atoms are always octahedrally surrounded by six Bi atoms. On the other hand a cubic environment for the Pt atoms is found in combination with the electron-deficient element lead in the compound  $\text{Pb}_4\text{Pt}$ .<sup>[26]</sup> Formulating  $\text{Bi}_{13}\text{Pt}_3\text{I}_7$  as  $([\text{Bi}_4\text{Pt}]_3)^{4+}(\text{BiI}_4)^-(\text{I}^-)_3$  gives every  $[\text{PtBi}_{8/2}]$  cube a charge of  $+4/3$ ; thus it is still far from being isoelectronic with the  $[\text{PtPb}_{8/2}]$  cube. Nevertheless, it seems that below a certain valence-electron concentration the cubic coordination for the Pt atom is favored.

The coordination number and mode change on moving from platinum to the lighter homologue nickel. The Bi/Ni system has already been mentioned above in connection with the subiodide  $\text{Bi}_{5.6}\text{Ni}_5\text{I}$ , which may be derived from the

intermetallic phase  $\text{Bi}_3\text{Ni}$ .<sup>[27]</sup> The other phase,  $\text{Bi}_3\text{Ni}$ , can also be partially oxidized using halogens. Here, care must be taken during the preparation to ensure that the temperature does not exceed the peritectic point of  $\text{Bi}_3\text{Ni}$ .

This method can be successfully used for the synthesis of the isostructural compounds  $\text{Bi}_{12.86}\text{Ni}_4\text{I}_6$ <sup>[28]</sup> and  $\text{Bi}_{12.86}\text{Ni}_4\text{Br}_6$ .<sup>[29]</sup> The characteristic building blocks of the intermetallic phase  $\text{Bi}_3\text{Ni}$  are conserved in their structures.<sup>[30]</sup> This involves monocapped trigonal prisms of Bi atoms, which are condensed through their two remaining uncapped rectangular faces to linear strings (Figure 7). As a consequence of the

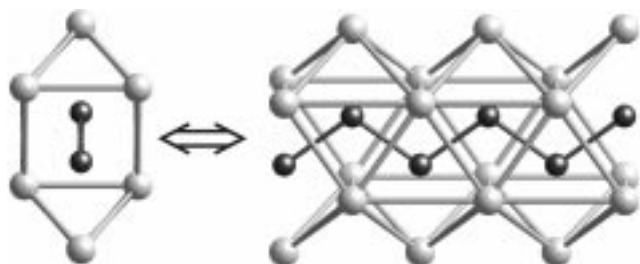


Figure 7. Two views of a prism string of composition  $[\text{NiBi}_{1/3}\text{Bi}_{2/3}]_{\infty} = \text{Bi}_3\text{Ni}$ .

prism condensation, the Ni atoms at the center of the Bi prisms form a zigzag chain. Although the Ni–Ni distances are comparatively short, they are nonbonding. These prism strings, corresponding to the composition  $[\text{NiBi}_{1/3}\text{Bi}_{2/3}]_{\infty} = \text{Bi}_3\text{Ni}$ , join together in a rod packing to give the intermetallic phase. In the subiodide  $\text{Bi}_{12}\text{Ni}_4\text{I}_3 = (\text{Bi}_3\text{Ni})_4\text{I}_3$  the prism strings are no longer close packed, but form porous double layers (Figure 8). Iodide ions fill the channels and separate the double layers.

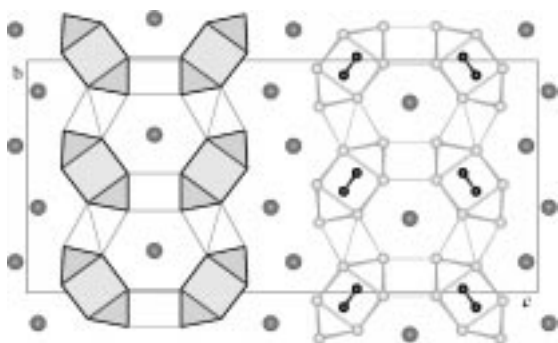


Figure 8. The crystal structure of  $\text{Bi}_{12}\text{Ni}_4\text{I}_3$ . The double layers consisting of  $\text{Bi}_3\text{Ni}$  prism strings are highlighted.

The halogen-richer subhalides of composition  $\text{Bi}_{12.86}\text{Ni}_4\text{X}_6 = (\text{Bi}_3\text{Ni})_4(\text{Bi}_{0.86}\text{X}_4)\text{X}_2$  ( $\text{X} = \text{Br}, \text{I}$ ) demonstrate an even smaller degree of connection between the intermetallic strings: deeply corrugated single layers are separated by isolated halide ions and halogenobismuthate groups (Figure 9). The nonstoichiometric formulation of the anions  $(\text{Bi}_{0.86}\text{X}_4)$  hides a complicated sequence of short chains of *trans*-edge-sharing  $[\text{BiX}_6]$  octahedra. Their varying lengths

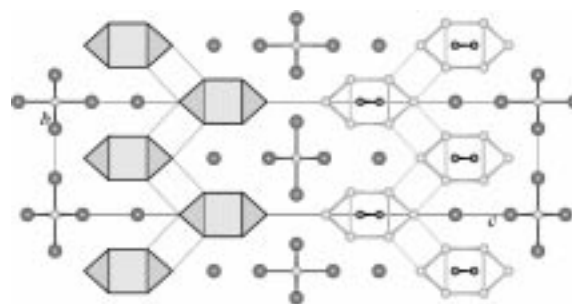


Figure 9. The crystal structure of  $\text{Bi}_{12.86}\text{Ni}_4\text{I}_6$ . Isolated iodide ions and oligomeric iodobismuthate(III) groups lie between deeply corrugated layers of  $\text{Bi}_3\text{Ni}$  prism strings.

manage the matching of the ionic and intermetallic parts of the structure.

As shown above, the contacts between the intermetallic strings become fewer with progressive oxidation, while the bond within a prism becomes stronger. This is demonstrated in the general shortening of the interatomic distances on going from  $\text{Bi}_3\text{Ni}$  to  $\text{Bi}_{12.86}\text{Ni}_4\text{X}_6$ . The variation in interatomic distances can be closely correlated to the changes in electron distribution (Table 1 and Figure 10). The oxidation leads to a drainage of electron density from the regions with metallic structure into the energetically low-lying states of the halogen atoms. Consequently, the energy states near the Fermi level, which are still occupied in  $\text{Bi}_3\text{Ni}$ , are emptied. Since these states possess antibonding character, the result of emptying

Table 1. Change in interatomic distances (in pm) on partial oxidation of  $\text{Bi}_3\text{Ni}$  with iodine.<sup>[a]</sup>

	$\text{Bi}_3\text{Ni}$	$\text{Bi}_{12}\text{Ni}_4\text{I}_3$	$\text{Bi}_{12.86}\text{Ni}_4\text{I}_6$
Bi–Bi	348	333	328
Ni–Ni	263	255	252

[a] Bi–Bi corresponds to the distance between the capping Bi atom and the four adjacent Bi atoms of a trigonal prism. Compare Figure 7 and 10.

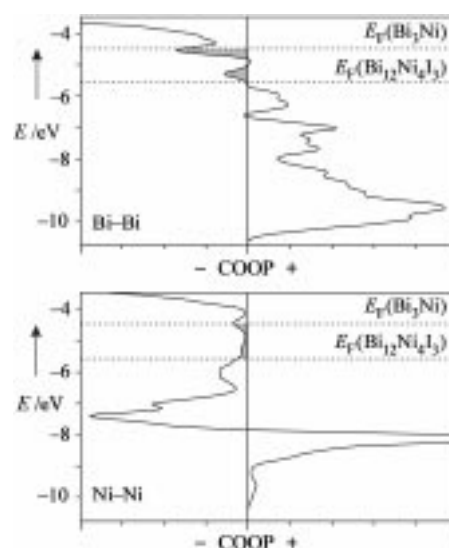


Figure 10. Emptying of the antibonding states through the lowering of the Fermi level ( $E_F$ ) on oxidation of  $\text{Bi}_3\text{Ni}$  to  $\text{Bi}_{12}\text{Ni}_4\text{I}_3$  (COOP = Crystal Orbital Overlap Population). See Table 1.

them is to produce a stronger chemical bond and shorter interatomic distances.

The modification of the electronic structure also affects the physical properties. Whilst  $\text{Bi}_3\text{Ni}$  can be described as non-magnetic,  $\text{Bi}_{12.86}\text{Ni}_4\text{I}_6$  undergoes a magnetic-ordering change from a Pauli paramagnet to a band ferromagnet at 25 K.

## 5. Quasi One-Dimensional Metals

The transition from a two- to a one-dimensional metal is already initiated for the subbromide  $\text{Bi}_{12.86}\text{Ni}_4\text{Br}_6$  and is fully established in another representative of the same ternary system: in the even more halogen-rich compound  $\text{Bi}_{6.86}\text{Ni}_2\text{Br}_5 = (\text{Bi}_3\text{Ni})_2(\text{Bi}_{0.86}\text{Br}_4)\text{Br}$  the  ${}^1_{\infty}[\text{NiBi}_{1/1}\text{Bi}_{6/3}]$  prism strings are entirely isolated from each other (Figure 11).<sup>[31]</sup>

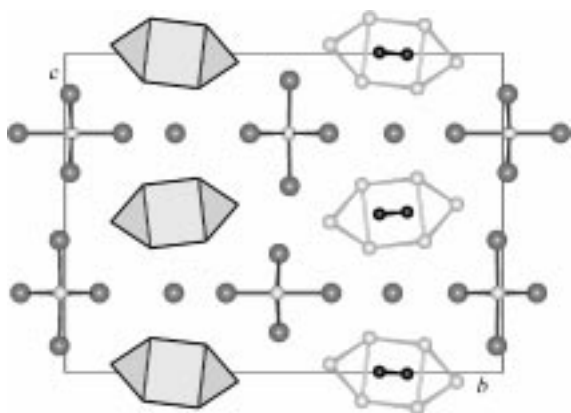


Figure 11. The incommensurate modulated crystal structure of  $\text{Bi}_{6.86}\text{Ni}_2\text{Br}_5$  drawn in a simplified form as one unit cell. The  $\text{Bi}_3\text{Ni}$  prism strings are separated by bromide and bromobismuthate(III) anions.

The problem of the metrical inequality between the rather rigid intermetallic string and the bromobismuthate(III) anions is solved here through the formation of an incommensurately modulated crystal structure. This can be modeled by imagining that the ionic structural units of formula  $(\text{Bi}_{0.86}\text{Br}_4)$  are made up of a complicated sequence of chains of varying lengths of *trans*-edge-sharing  $[\text{BiBr}_6]$  octahedra that alternate between two orientations.

Clearly, only the electrons within the metallic bonding system of the 1D polyhedron strings show mobility. Still it is better to describe these as *quasi* one-dimensional metals, since according to the Peierls theorem completely one-dimensional metals should not exist, and here we are discussing three-dimensional, albeit strongly anisotropic solids.

That such compounds can indeed still possess metallic conductivity is demonstrated in the compound  $\text{Bi}_9\text{Ir}_2\text{I}_3$  (Figure 12).<sup>[32]</sup> This subiodide along with  $\text{Bi}_9\text{Rh}_2\text{I}_3$  and  $\text{Bi}_9\text{Rh}_2\text{Br}_3$  are members of a small group of compounds that although having the same stoichiometries are not isostructural. Their common structural feature is the form of the intermetallic part of the structure which is made up of isolated  ${}^1_{\infty}[\text{MBi}_{1/1}\text{Bi}_{7/2}]$  polyhedral strings (Figure 13). In these, each metal (M) atom is surrounded by eight Bi atoms, which form a bicapped

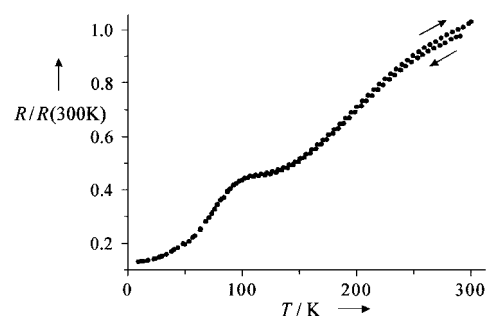


Figure 12. Temperature dependence of the electrical resistance of the quasi one-dimensional metal  $\text{Bi}_9\text{Ir}_2\text{I}_3$ .

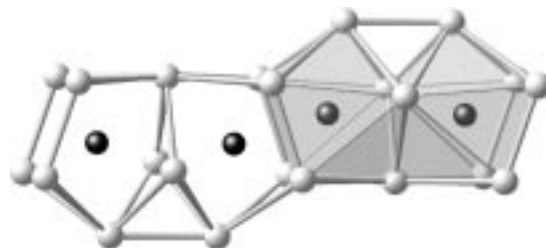


Figure 13. The slightly wavy string of face-sharing  $[\text{MBi}_{1/1}\text{Bi}_{7/2}]$  polyhedra in  $\text{BiM}_2\text{X}_3$ .

trigonal prism. The polyhedra are linked through the triangular and rectangular faces.

The simplest structural variant for the strings is found in  $\text{Bi}_9\text{Rh}_2\text{I}_3$  where all the strings point in the same direction. In  $\text{Bi}_9\text{Rh}_2\text{Br}_3$  and  $\text{Bi}_9\text{Ir}_2\text{I}_3$  two orientations alternate in layers with a strict 2-1 or 2-2 sequence of the layers (Figure 14). The structural differences among the three packing types can be clearly seen: the  ${}^1_{\infty}[\text{MBi}_{1/1}\text{Bi}_{7/2}]$  strings must have a significant influence on the translational period parallel to them. Since one is fixed by the intermetallic structural part, it is necessary to use the two other directions to accommodate the different space requirements of the bromide and iodide ions.

At this point, it is worth considering the remarkable crystal chemistry of the anions. In all the ternary bismuth subhalide structures discussed so far, the halide ions have had eight to twelve Bi atoms as nearest neighbors. Such high coordination numbers for anions are very unusual, though comparable coordination numbers (CN) are observed in metal-rich subsulphides like  $\text{Ta}_6\text{S}^{[33]}$  with  $\text{CN}(\text{S}) = 7$  and  $\text{V}_3\text{S}^{[34]}$  with  $\text{CN}(\text{S}) = 10$ . From this point of view, the anions behave as if they were the third component of a ternary alloy. This feature no longer applies to the following compounds, where the halide ions adopt the more typical two- or threefold bridging positions. Examples for this are found in the columnar structures of  $\text{Bi}_4\text{RuBr}_2$  and  $\text{Bi}_4\text{RuI}_2$ .<sup>[35]</sup> Both structures, which differ only in small details, consist of infinite strings of face-sharing square  $[\text{RuBi}_{8/2}]$  antiprisms (Figure 15). The edges of alternate  $\text{Bi}_4$  squares within a string are bridged by halide ions. The Ru atoms lying along the central axis are not arranged in an equidistant fashion, but instead form pairs. Using band-structure calculations it was shown that the comparatively short Ru–Ru distance is not the result of a direct bond as a consequence of Peierls distortion, but rather the result of strong bonds between the Ru atoms and the Bi atoms of the

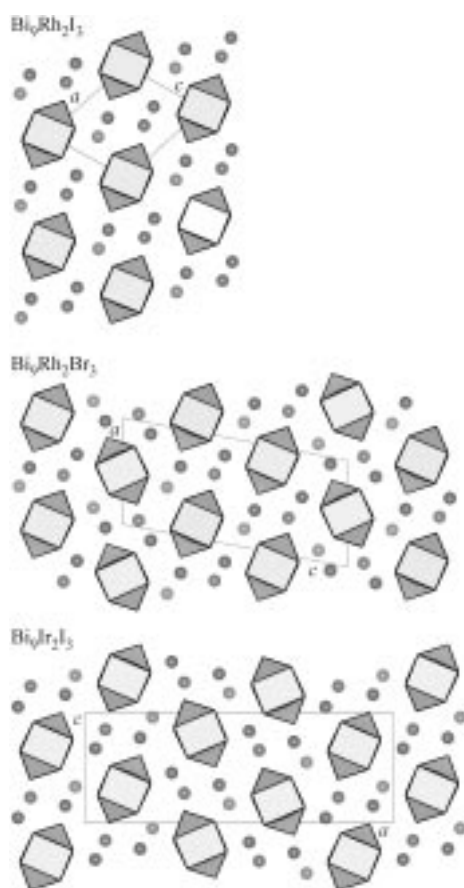


Figure 14. Different spatial arrangements of  $\infty^1[\text{MBi}_{1/3}\text{Bi}_{7/3}]$  polyhedra strings in  $\text{Bi}_9\text{Rh}_2\text{I}_3$ ,  $\text{Bi}_9\text{Rh}_2\text{Br}_3$ , and  $\text{Bi}_9\text{Ir}_2\text{I}_3$ .

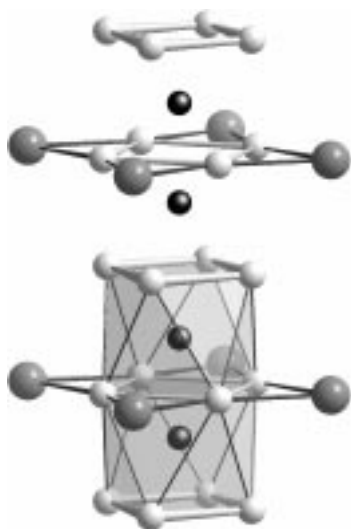


Figure 15. String of face-sharing square  $[\text{RuBi}_{8/2}]$  antiprisms in the columnar structures of  $\text{Bi}_4\text{RuBr}_2$  and  $\text{Bi}_4\text{RuI}_2$ . The edges of the larger  $\text{Bi}_4$  squares are bridged by halide ions.

halide-bridged  $\text{Bi}_4$  squares, which are about three times as strong as the bonds to the halide-free  $\text{Bi}_4$  squares.

The crystal structures of  $\text{Bi}_4\text{RuBr}_2$  and  $\text{Bi}_4\text{RuI}_2$  can be regarded as defect structures of the  $\text{W}_5\text{Si}_3$  type. Here the Bi atoms occupy the cation sites whilst the two crystallographically different lattice sites of the silicide anions are occupied

by the halide ions and the Ru atoms, respectively. This remarkable analogy in crystal chemistry gives an indication of the electronic situation of the Ru atoms in the above-mentioned subhalides.

## 6. Ionic and Molecular Clusters

If we again apply the “chemical scissors” of oxidation to  $\text{Bi}_4\text{RuBr}_2$  using bromine the 1D intermetallic string can be cut into pieces. The result is a significantly halogen-richer subbromide of formula  $\text{Bi}_{24}\text{Ru}_3\text{Br}_{20}$ .<sup>[36]</sup> The isostructural chloride  $\text{Bi}_{24}\text{Ru}_3\text{Cl}_{20}$  as well as mixed crystals of both compounds are also known.<sup>[37]</sup>

The aforementioned snippets of the  $\infty^1[\text{RuBi}_{8/2}]$  string enclose three face-sharing square antiprisms of Bi atoms (Figure 16). The stack is terminated on one side by a single Bi atom and contains only two Ru atoms; four bromide ions

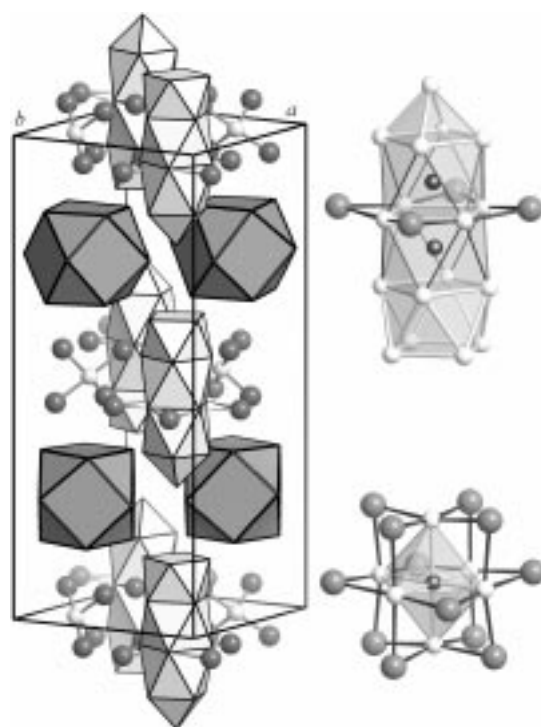


Figure 16. The crystal structure of  $\text{Bi}_{24}\text{Ru}_3\text{Br}_{20}$ . The cuboctahedra  $[\text{RuBi}_6\text{Br}_{12}]^{2-}$  cluster and the  $[\text{Ru}_2\text{Bi}_{17}\text{Br}_4]^{3+}$  stacks are shown in detail.

surround the central four-membered ring of Bi atoms. An alternative description of the arrangement of atoms in the  $[\text{Ru}_2\text{Bi}_{17}\text{Br}_4]$  stack involves the segregation into a square antiprism of  $\text{Bi}_8^{2+}$  ions, a square-based pyramid of  $\text{Bi}_5^+$  ions, and the  $[\text{Ru}_2\text{Bi}_4\text{Br}_4]$  central unit. The assignment of the charges on the polycations is based on modified Wade’s rules, in which each Bi atom contributes three 6p electrons to the bonding in the cluster.<sup>[38]</sup> The  $\text{Bi}_5$  pyramid has the appearance of a *nido* cluster and consequently should be stable with 14 cluster electrons (CE), leading to an overall charge of +1. Analogously, the  $\text{Bi}_8^{2+}$  square antiprism forms an *arachno* cluster (22 CE), and the  $\text{Bi}_5^{3+}$  trigonal bipyramid described in the Introduction (see Figure 2) a *closo* cluster (12 CE).



In  $\text{Bi}_{24}\text{Ru}_3\text{Br}_{20}$  the charge compensation is reached through two different anionic components: cuboctahedral  $[\text{RuBi}_6\text{Br}_{12}]^{2-}$  cluster and  $[\text{BiBr}_4]^-$  groups. Within the  $[\text{RuBi}_6\text{Br}_{12}]^{2-}$  clusters, six Bi atoms coordinate the central Ru atom octahedrally (Figure 16); bromide ions bridge the twelve edges of the octahedron. Whilst the short Bi–Ru contacts can be mainly described as covalent single bonds, the edge lengths of the octahedra preclude any significant interaction between the Bi atoms.

A comparison with the crystal structure of BiBr is highly informative: in the  $[\text{RuBi}_6\text{Br}_{12}]^{2-}$  cluster each Bi atom is coordinated by four bridging Br atoms and perpendicular to these by an Ru atom. In the chain-structure of  $\text{BiBr} = (\text{Bi}^0(\text{Bi}^{\text{II}})\text{Br}_{4/2})$ , each outer  $\text{Bi}^{\text{II}}$  is bonded to four bridging Br atoms in addition to a perpendicular inner  $\text{Bi}^0$  atom (see Figure 1). Thus, the  $(\text{Bi}^{\text{II}}\text{Br}_2)$  partial structures in BiBr and in  $[\text{RuBi}_6\text{Br}_{12}]^{2-}$  clusters have the same relationship to each other as the chain structure of  $\alpha\text{-PdCl}_2$  and the cluster structure of  $\beta\text{-PdCl}_2$ .<sup>[39]</sup> Formally, it is possible to separate the  $[\text{RuBi}_6\text{Br}_{12}]^{2-}$  ion into a neutral  $(\text{Bi}^{\text{II}}\text{Br}_2)_6$  shell and an internal Ru atom with a  $-II$  oxidation state. By using the electron-counting rules of complex chemistry we expect that with six Bi–Ru bonds there is a total of 16 valence electrons (VE) on the central atom. Although no definitive statement concerning the actual charge distribution can be made, the suggestion of a partial negative charge on the Ru atom is supported by the topology of the  $[\text{RuBi}_6\text{Br}_{12}]$  cluster: the cluster corresponds to a portion of the NaCl lattice, in which Ru and Br atoms both occupy the anion positions. In addition, many examples of similarly constructed clusters can be cited, in which interstitial atoms surrounded by positively charged atoms must clearly be described as possessing anionic character.<sup>[4, 40]</sup>

The subhalides  $\text{Bi}_{14}\text{Si}_2\text{MI}_{12}$  and  $\text{Bi}_{12-x}\text{MX}_{13-x}$  represent the final step in the transition from extensive intermetallic and saltlike areas to an ionic lattice of small charged units, along which  $\text{Bi}_{24}\text{Ru}_3\text{Br}_{20}$  with its oligomeric  $[\text{Ru}_2\text{Bi}_{17}\text{Br}_4]$  cluster stacks represent an intermediate state. The arrangement of the ionic building blocks in  $\text{Bi}_{14}\text{Si}_2\text{MI}_{12}$  and in  $\text{Bi}_{12-x}\text{MX}_{13-x}$  display the CsCl structure type.

The two quaternary phases with the formula  $[\text{Bi}_{14}\text{Si}_2\text{MI}_{12}]$  ( $M = \text{Rh}, \text{Ir}$ ) consist of  $[\text{Bi}_8\text{Si}_2]^{3+}$  ions and  $[\text{MBi}_6\text{I}_{12}]^{3-}$  ions (Figure 17).<sup>[41]</sup> The assignment of the charges comes from a band-theory treatment which reveals that all the bonding or nonbonding orbitals of the cuboctahedral  $[\text{MBi}_6\text{I}_{12}]^{3-}$  cluster should be filled (18 VE for M). The  $[\text{Bi}_8\text{Si}_2]^{3+}$  polyhedron consists of a square antiprism of Bi atoms with each of the square faces capped by an Si atom. Thus, the cation is topologically equivalent to the molecule 1,10-dicarba-*closo*-decaboran(10)<sup>[42]</sup> and to the anionic cluster *closo*- $[\text{Li}_2\text{Sn}_8]^{4-}$ .<sup>[43]</sup> Unlike them, the  $[\text{Bi}_8\text{Si}_2]^{3+}$  cation has three cluster electrons more than would be expected for a *closo* polyhedron (22 CE) according to Wade's rules. The double degeneracy of the antibonding HOMO, which contains the three surplus electrons, is abolished by a small but detectable distortion of the  $[\text{Bi}_8\text{Si}_2]^{3+}$  ion (Jahn–Teller distortion).

The ionic description as a cluster salt corresponds to the semiconducting nature of  $\text{Bi}_{14}\text{Si}_2\text{IrI}_{12}$ . However, a small thermal activation is sufficient to overcome the band gap of

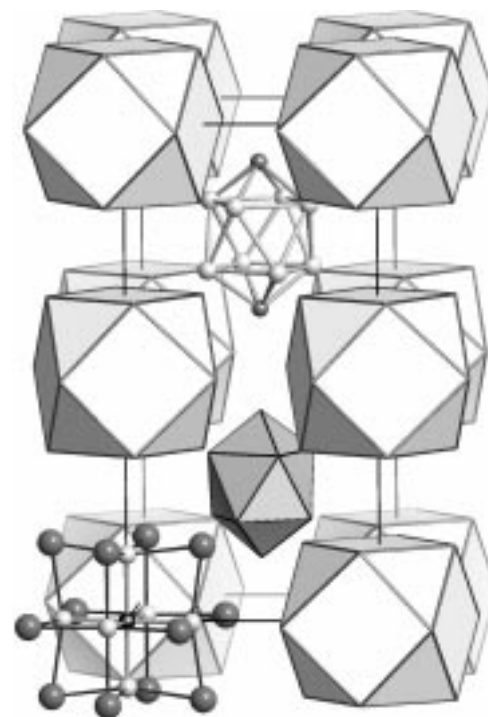


Figure 17. The crystal structure of  $\text{Bi}_{14}\text{Si}_2\text{IrI}_{12}$  with  $[\text{Bi}_8\text{Si}_2]^{3+}$  polyhedra and  $[\text{IrBi}_6\text{I}_{12}]^{3-}$  cuboctahedra.

about 0.1 eV and thereby mobilize the electrons. The magnetic properties of  $\text{Bi}_{14}\text{Si}_2\text{IrI}_{12}$  are of note: the paramagnetism of the unpaired electrons is overlaid by such a dominant diamagnetic component that the susceptibility remains in the negative region even to very low temperatures (Figure 18).

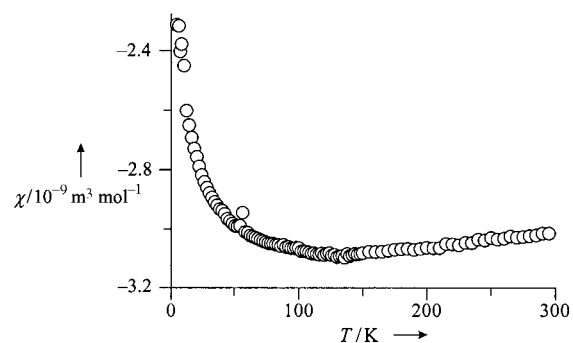


Figure 18. Temperature dependence of the molar magnetic susceptibility of  $\text{Bi}_{14}\text{Si}_2\text{IrI}_{12}$ .

The subhalides of average formula  $\text{Bi}_{12-x}\text{MX}_{13-x}$  ( $M = \text{Rh}, \text{Ir}$ ;  $X = \text{Cl}, \text{Br}$ ;  $x < 1$ ) show a phase range, because of tiny changes of the relative proportions of the building units.<sup>[44]</sup> These building blocks include the homonuclear polycations  $\text{Bi}_5^+$  and  $\text{Bi}_6^{2+}$  as well as the cluster anions  $[\text{MBi}_6\text{X}_{12}]^-$  and  $[\text{MBi}_6\text{X}_{13}]^{2-}$  (Figure 19). Whilst the square-based pyramidal  $\text{Bi}_5^+$  ion with 14 CE can easily be classified as a *nido* cluster, with the distorted “octahedral”  $\text{Bi}_6^{2+}$  ion things are not so simple. The seeming contradiction between the 16 CE, which suggest a *nido* cluster, and the apparently closed cage is resolved on closer examination: the shape of the  $\text{Bi}_6^{2+}$  cation

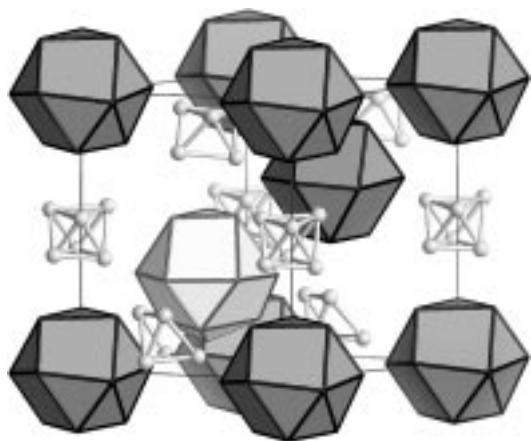


Figure 19. Crystal structure of  $\text{Bi}_{11.67}\text{IrBr}_{12.67} = \text{Bi}_{34}\text{Ir}_3\text{Br}_{37}$  with  $\text{Bi}_5^+$  and  $\text{Bi}_6^{2+}$  polycations as well as  $[\text{IrBi}_6\text{Br}_{12}]^{2-}$  cubooctahedra (shaded) and  $[\text{IrBi}_6\text{Br}_{13}]^{2-}$  clusters (light).

deviates significantly from that of a regular octahedron so that it is as if a seventh atom has been removed from a hypothetical *closo* cluster.

As expected, the subbromide  $\text{Bi}_{11.67}\text{IrBr}_{12.67} = \text{Bi}_{34}\text{Ir}_3\text{Br}_{37}$  is a diamagnetic semiconductor with a substantial electric resistance. The black color of the compound indicates that the band gap must lie below the energy of visible light.

The unexpected termination to the series of known ternary bismuth subhalides occurs with the compound  $\text{Bi}_7\text{RhBr}_8$ .<sup>[45]</sup> This subbromide no longer consists of bismuth polycations and cluster anions but rather of a single type of uncharged unit (Figure 20). Even in the  $[\text{RhBi}_7\text{Br}_8]$  molecules the differing electronic requirements of the components are manifested. Two apparently incompatible coordination geometries sit side-by-side: a pentagonal bipyramid about the central Rh atom and an almost square-planar coordination of the apical Bi atoms by bromide ions.

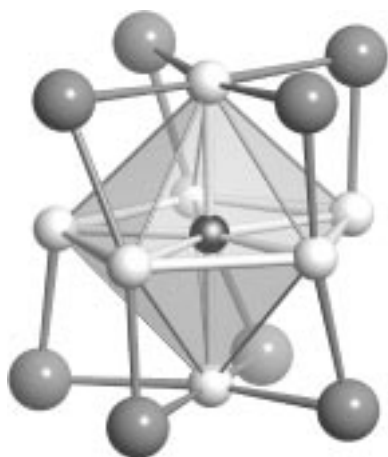


Figure 20. Molecular  $[\text{RhBi}_7\text{Br}_8]$  cluster.

The bonding is also correspondingly difficult to understand: from *ab initio* calculations we expect that the Bi atoms in the central five-membered ring are bonded to each other through 5-center-4-electron bonds.<sup>[46]</sup> Assuming that a) the seven Bi atoms are bound by single covalent bonds to the Rh atom and b) the square-planar coordinated apical Bi atom can be

assigned the oxidation state +II, we can formulate  $\text{Bi}_7\text{RhBr}_8$  as  $(\text{Bi}_5^{\text{VI}})(\text{Bi}^{\text{II}})_2\text{Rh}^{\text{II}}(\text{Br}^{\text{I}})_8$  with 18 VE for the transition metal.

## 7. Conclusion and Outlook

Intermetallic phases of bismuth and a transition metal from Groups 8–10 can be partially oxidized with halogens. In the resulting ternary subhalides the mobility of the conducting electrons becomes more restricted with increasing oxidation. The resulting range of compounds stretches from “porous” three-dimensional metals, that are interspersed with anions ( $\text{Bi}_{5.6}\text{Ni}_5\text{I}$ ,  $\text{Bi}_{12}\text{Rh}_3\text{Br}_2$ ), through two-dimensional ( $\text{Bi}_{13}\text{Pt}_3\text{I}_7$ ,  $\text{Bi}_{12}\text{Ni}_4\text{I}_3$ ,  $\text{Bi}_{12.86}\text{Ni}_4\text{X}_6$ ) and one-dimensional systems ( $\text{Bi}_{6.86}\text{Ni}_2\text{Br}_5$ ,  $\text{Bi}_9\text{M}_2\text{X}_3$ ,  $\text{Bi}_4\text{RuX}_2$ ), to semi-conductors with very small ( $\text{Bi}_{14}\text{Si}_2\text{MI}_{12}$ ) or moderately large band gaps ( $\text{Bi}_{24}\text{Ru}_3\text{X}_{20}$ ,  $\text{Bi}_{12-x}\text{MX}_{13-x}$ ,  $\text{Bi}_7\text{RhBr}_8$ ).

The synthetic possibilities offered by using chlorine and fluorine on the intermetallic phases are yet to be explored. Since these halogens are more oxidizing, we can expect to see cluster salts with even higher halogen contents and with band gaps falling in the visible region.

In the general phase diagram (Figure 21), the subhalides described above are grouped in the phase area that lies

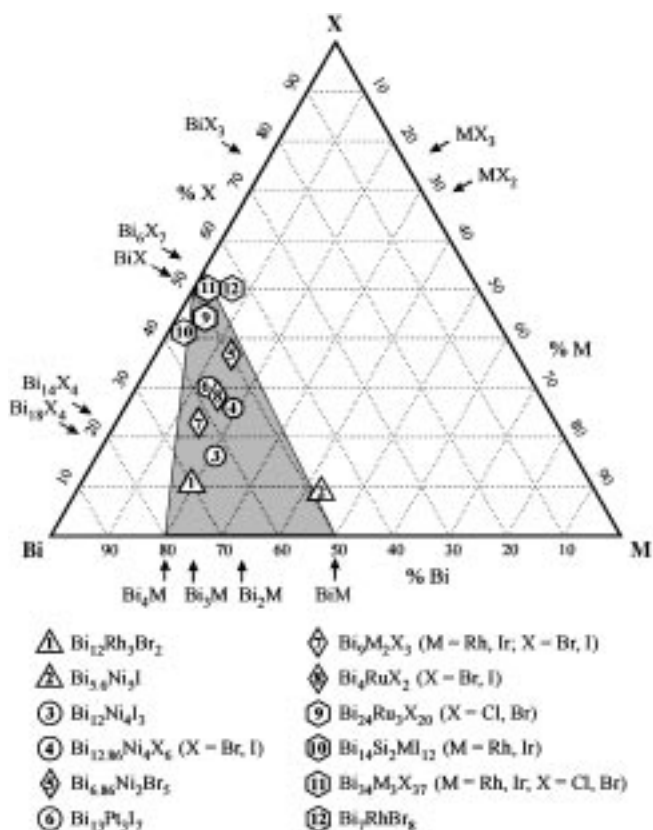


Figure 21. Generalized phase diagram of the ternary system bismuth, transition metal (M), and halogen (X) showing the known ternary phases. The bismuth and silicon components for the quaternary compounds  $\text{Bi}_{14}\text{Si}_2\text{MI}_{12}$  are combined. The symbols indicate for the intermetallic structural part whether it is three-dimensional (triangle), two-dimensional (circle), one-dimensional (diamond) or made up of isolated clusters (hexagon).

between the pseudo-binary "intersections"  $\text{BiX}-\text{Bi}_4\text{M}$  and  $\text{Bi}_6\text{X}_7-\text{BiM}$ . The bismuth content varies between 70 at. % in  $\text{Bi}_{12}\text{Rh}_3\text{Br}_2$  and 44 at. % in  $\text{Bi}_7\text{RhBr}_8$ , the halogen content between 12 at. % in  $\text{Bi}_{5,6}\text{Ni}_5\text{I}$  and 50 at. % in  $\text{Bi}_7\text{RhBr}_8$ . The trend is that a higher halogen content is linked to a lower transition metal content without, however, there being a true correlation between the ratios of the elements.

For all the currently known compounds it is the case that the halide ions have no direct contact to the transition metals, but rather are exclusively bonded to the Bi atoms. As a result, a higher halogen content leads to a larger surface area of the intermetallic structural region formed by the Bi atoms. In this way, the ordering of the subhalides according to increasing oxidation state corresponds to the ordering in terms of increasing penetration of intermetallic and saltlike structural regions.

The decrease of the intermetallic structural regions with increasing degree of oxidation leads inevitably to a gradual change in the chemical bonding. The metallic bonding which is present in the particularly halogen-deficient compounds and stretches in one, two, or, three dimensions through the crystal is replaced by the many-centered bonds in isolated clusters and finally turns into covalent single bonds between the transition metal and the bismuth atoms.

The strong bonding within the areas of the structure built up from metal atoms is an important factor in stabilizing the ternary bismuth subhalides. This is true not only for the intermetallic strings discussed in detail above for the subhalides  $\text{Bi}_{12}\text{Ni}_4\text{I}_3$ ,  $\text{Bi}_{12,86}\text{Ni}_4\text{X}_6$ , and  $\text{Bi}_{6,86}\text{Ni}_2\text{Br}_5$  derived from  $\text{Bi}_3\text{Ni}$ , but also for the various types of cluster. The stability of the chemical bonds is reflected by the remarkable chemical inertness observed in the bismuth subhalides.

In view of the relatively robust and largely isolated building blocks in the solid state, the question arises as to the whether these could be stabilized in solution through the use of bulky ligands as has been observed for aluminum,<sup>[47]</sup> gallium,<sup>[48]</sup> and indium<sup>[49]</sup> clusters. Experiments to synthesize ligand-stabilized bismuth clusters starting from  $\text{Bi}_6\text{Br}_7$  have recently led to the tetramer  $[\text{Bi}(\text{Si}(\text{SiMe}_3)_3)]_4$ .<sup>[50]</sup> Such four-membered rings made up of Bi atoms are, however, also accessible using other routes.<sup>[51]</sup>

The question regarding the valencies of the transition metal atoms in ternary subhalides is still to be resolved. Crystal chemistry and bonding theory both indicate that, contrary to conventional ideas, negative oxidation states occur: apparently transition metals and halide ions repel one another in the crystal structures of the subhalides and are shielded from each other by the positively charged Bi atoms. There are also various structural parallels to well-known, heteropolar compounds (e.g.  $\text{NaCl}$  or  $\text{W}_5\text{Si}_3$ ) which show that the transition metals in the ternary bismuth subhalides occupy the typical anion positions in such structures.

This point of view is further supported by population analyses based on extended Hückel calculations, which assign partial negative charges to the transition metals in all these compounds. It is possible that the driving force for this is that the relatively electron-rich elements of Groups 8–10 can complete their shells by only taking up a few extra electrons (to give  $s^0d^{10}$  or  $s^2d^{10}$  configurations or else, 16 or 18 VE

according to electron-counting rules). To shed further light on the problem, comparative Mößbauer spectroscopy studies on the iridium-containing subvalent compounds of bismuth, tin, and indium as well as related intermetallic phases are underway. In parallel, quantum mechanical calculations using density functional theory should give a more reliable picture of the chemical bonding.

A further characteristic of the crystal structures of nearly all the ternary bismuth subhalides is the inherent pseudo symmetry. This is because the symmetry of the intermetallic structural part cannot be applied to the whole structure. The discrepancy between the high symmetry of substantial portions of the structure and the significantly lower symmetry of the total structure leads to many crystallographic problems, which have been extensively discussed elsewhere.<sup>[31]</sup>

The particular appeal of the bismuth subhalide class of substances lies in their highly differentiated structures and bonding relationships. In view of the individual and, in practically all cases, novel solutions to achieve the optimum bonding situation in the solid state, demonstrated for all of the ternary systems described here, it is virtually impossible to predict the composition or crystal structures of yet to be discovered representatives. The discovery of unusual new subhalides can certainly be expected.

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