Zintl Phases

Introduction

"Zintl Phases" stand somewhere in-between metallic and ionic compounds. They were named "Zintl Phases" after Edward Zintl who pioneered their structures.

A typical Zintl phase is NaTl. Although the composition of NaTl sounds very similar to NaCl, the structure is completely different. The difference is that the anions don't reach the octet as isolated species, they need additional bonds. In the case of NaTl every Tl^--ion is covalently connected to 4 neighbored Tl^--ions. The anionic partial structure is comparable to the diamond structure.

Definition & Properties

Zintl phases…

1. contain an alkali or alkaline-earth metal and a p-element (or elements) that is a metal, semimetal, or small-gap semiconductor;
2. tare electronically balanced or closed-shell compounds, i.e. the number of electrons provided by the constituting elements equals the number of electrons needed for covalent bonding in the structure;
3. obey the 8-N rule **(N is the number of the outer shell electrons of the anion!)**
4. thave very narrow or no homogeneity width, i.e. they are line compounds;
5. are semiconductors or poor conductors;
6. are diamagnetic or show very weak, temperature- independent para magnetism;
7. are brittle.

Examples:

K_4Ge_4

number of outer shell electrons of the anion: 5

→ every ion forms 3 covalent bonds (comparable to the structure of an element with 5 outer shell electrons)

in K_4Ge_4 Ge forms isolated $(Ge_4)^{4-}$ ions (comparable to white phosphorus)

CaSi

number of outer shell electrons of the anion: 6

→ every ion forms 2 covalent bonds (comparable to the structure of an element with 6 outer shell electrons)

in CaSi Ge forms $(Si_n)^{2n-}$ chains (comparable to grey selenium)

Ba_3Si_4

number of outer shell electrons of the anion: 5,5

→ 2 Si with 6 outer shell electrons (2-bonded) and two Si with 5 outer shell electrons (3-bonded)

in Ba_3Si_4 Si forms $(Si_4)^{6-}$ butterfly anions

References:

- Ulrich Müller, Inorganic Structural Chemistry, Second edition 1992, page 116-120
- ssevov-g5.chem.nd.edu/articles/SlaviChapter.pdf