Zintl phases

Introduction

- Typical **Ionic solids** are formed between alkali and alkaline earth metals and non-metal elements from the chalcogen and halogen groups. e.g. NaCl, CsCl, CaF_2…
- **Covalent bonds** are formed between non-metal elements. e.g. H_2, H_2O, CO_2, CH_4...
- **Zintl phases** are arranged in-between these two types of chemical bonds.

Definition

Zintl phases are compounds formed by metals with a low electronegativity (alkali and alkaline earth group) and elements with an intermediate electronegative (group 13 – 15).

Zintl-Klemm-Concept

In an Zintl phase the metal donates one or more electrons to the electronegative element. The anions behave as elements of the group with the same valence electron configuration. They form substructures which are typical for elements of the corresponding group.

VEC

The **v**alence **e**lectrons **c**oncentration (VEC) of the anions can be calculated by the following equation:

$$\boxed{VEC = [m \cdot e(M) + x \cdot e(X)]/x}$$

m = number of the cations per chemical formula
n = number of the anions per chemical formula
e(M), e(X) = number of valence electrons of the respective elements

With the VEC we can calculate the number of covalent bonds formed by the anions:

$$\boxed{b(XX) = 8 - VEC}$$

The results of these two equations give hints for the correct structure.

Examples

NaTl
VEC = $[1 \cdot 1 + 1 \cdot 3]/1 = \underline{4}$ → the anion acts as an element of group 14.
b(XX) = $8 - 4 = \underline{4}$ → Tl^- ions form 4 covalent bonds.
A structure analyse shows that Tl^- forms a diamond-like structure.

K_4Ge_4
VEC = $[4 \cdot 1 + 4 \cdot 4]/4 = \underline{5}$ → the anion acts as an element of group 15.
b(XX) = $8 - 5 = \underline{3}$ → Ge^- ions forms 3 covalent bonds .
A structure analyse shows that Ge^- forms $(Ge_4)^{4-}$ tetrahedra (comparable to white phosphorous, P_4).

Properties of Zintl phases

- many Zintl phases are brittle and deeply coloured or they show metallic luster
- many Zintl phases are semi-conductors
- they are sensitive against water and oxygen
- they have high melting points
- Zintl phases with smaller anions are soluble in liquid ammonia
- they have fixed composition

Synthesis of Zintl phases

Some Zintl phases ca be synthesized in liquid ammonia where the element of group 13 – 15 reacts with the less electronegative metals. A second possibility is the direct synthesis from the elements.

Questions

1. Calculate the VEC and b(XX) for Ba_3Si_4. Suggest an anionic partial structure. How is the anion called?
2. Calculate the VEC and b(XX) for $SrGa_2$. Suggest different types of anionic partial structures?

Literature

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